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US Army Research Laboratory

US Army Research Laboratory Lightweight and Specialty Metals Branch Research and Development (FY14)

by Mark A Tschopp and Heidi E Maupin

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14. ABSTRACT
The Lightweight and Specialty Metals Branch (LSMB) lies within the Materials and Manufacturing Science Division of the Weapons and Materials Research Directorate of the US Army Research Laboratory (ARL). LSMB's mission is to perform the fundamental and applied research and development in metals to create transformational metallic systems to enable battlefield overmatch; and to protect and defend our country by empowering, unburdening, and safeguarding our servicemen and women. LSMB's vision is to be the leading metals research and development facility for the US Army, which is achieved by attracting and retaining world-class researchers with exceptional credentials; building the necessary infrastructure for metals research; and integrating research with Army-relevant applications to enable game-changing, competitive capability. LSMB's strategy is to balance in-house capability, talent, resources, and infrastructure with external agencies/facilities to drive foundational materials research that meets the needs of the US Army. This report is a summary of published research within FY14 for LSMB.

15. SUBJECT TERMS journal publications, technical reports, lightweight metals, specialty metals, processing, microstructure, properties, alloy design

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Contents

List of Figures iv

List of Tables v

Acknowledgments vi

1 Lightweight and Specialty Metals Branch 1

1.1 LSMB Mission 1

1.2 LSMB Vision 2

1.3 LSMB Strategy 2

1.4 LSMB Core Values 2

1.5 LSMB Core Competencies 3

1.6 Personnel 4

2 FY14 Research and Development Summary 6

2.1 LSMB Selected Highlights 6

2.2 Refereed Journal Papers 8

2.3 ARL Technical Publications 11

Appendix A. FY14 Journal Publications 15

Appendix B. FY14 ARL Technical Publications 45

List of Symbols, Abbreviations, and Acronyms 55

Distribution List 56

List of Figures

Fig. 1 Lightweight and Specialty Metals Branch within the Materials and Manufacturing Science Division of ARL 1

Fig. 2 LSMB at the US Army Research Laboratory 4

List of Tables

Table LSMB Metallurgy and Materials Core Competencies 3

Acknowledgments

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1. Lightweight and Specialty Metals Branch

The US Army Research Laboratory (ARL) of the US Army Research Development and Engineering Command (RDECOM) is the Army's corporate, or central, laboratory. Its diverse assortment of unique facilities and dedicated workforce of government and private sector partners make up the largest source of world-class integrated research and analysis in the Army. ARL's mission is to discover, innovate, and transition science and technology to ensure dominant strategic land power. ARL's vision is to be the nation's premier laboratory for land forces.

The Lightweight and Specialty Metals Branch (LSMB) lies within the Materials and Manufacturing Science Division of the Weapons and Materials Research Directorate of ARL.

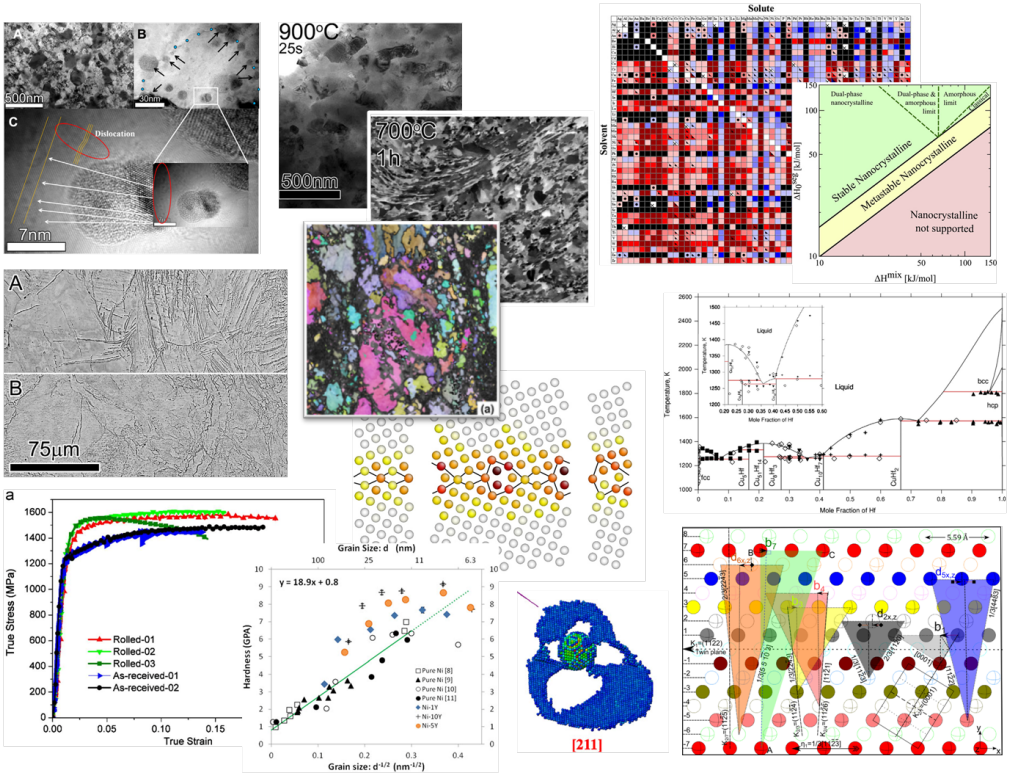

Fig. 1 Lightweight and Specialty Metals Branch within the Materials and Manufacturing Science Division of ARL

1.1 LSMB Mission

The LSMB mission is to perform the both fundamental and applied research and development in metals to create transformational metallic systems to enable battlefield overmatch; and to protect and defend our country by empowering, unburdening, and

safeguarding our servicemen and women.

1.2 LSMB Vision

The LSMB vision is to be the leading metals research and development facility for the US Army. This vision is achieved by attracting and retaining world-class researchers with exceptional credentials; building the necessary infrastructure for metals research; and integrating research with Army-relevant applications to enable game-changing, competitive capability that is unique in comparison to external academic, industrial, and government facilities.

1.3 LSMB Strategy

The LSMB strategy is to balance in-house capability, talent, resources, and infrastructure with external agencies/facilities to drive foundational materials research that meets the needs of the US Army.

1.4 LSMB Core Values

The LSMB core values are:

1) **Agility**. LSMB is nimble. LSMB is composed of researchers with expertise in alloy development, metal processing, microstructure characterization, property evaluation, and performance of protection/lethality systems, who are cross-trained and prepared to adapt to a dynamically-changing research field.

2) **Synergy**. LSMB has a strong culture of collaboration and alliances among branches and other divisions, which allows LSMB to pursue multidisciplinary research efforts for the mission of the US Army while providing customer support to those who wish to leverage LSMB's metals expertise.

3) **Integrity**. LSMB advocates strong ethical responsibility, and a resounding show of respect for each other's strengths. LSMB researchers take responsibility of safety for ourselves and each other, and understand associated risks during operations as we promote the use of environmentally-healthy materials.

4) **Pride**. LSMB performs decidedly cross-cutting foundational research to produce next generation materials.

1.5 LSMB Core Competencies

The LSMB core competencies are based on the foundations of metallurgical science and engineering (below): 1) Lightweight and Structural Metals, 2) Specialty Metals Processing and Synthesis, 3) Multiscale Structure-Property Characterization, and 4) Integrated Computational Materials Design and Engineering.

Table LSMB Metallurgy and Materials Core Competencies

Lightweight and Structural Metals for Protection and Lethality	1. Aluminum alloys 2. Magnesium alloys 3. Ferrous alloys 4. Tungsten alloys 5. Nanocrystalline materials 6. Hierarchical Composite Materials 7. Multifunctional Materials 8. Functionally-Graded Materials
Specialty Metals Processing and Synthesis	1. Rare Earth Metals 2. Extractive Metallurgy 3. Process Technology and Modeling 4. Powder Processing and Synthesis 5. Surface Engineering and Treatments 6. Welding and Joining Technology 7. Severe Plastic Deformation 8. Electrodeposition and Vapor Deposition 9. Solidification and Casting 10. Heat Treatment
Multiscale Structure-Property Characterization	1. Physical and Mechanical Metallurgy 2. Microscopy and Materials Characterization 3. Mechanical Behavior of Materials 4. Deformation Mechanisms 5. Corrosion and Environmental Effects 6. Fatigue, Damage, and Fracture
Integrated Computational Materials Engineering (Materials-By-Design)	1. Material Modeling (Atomistic to Mesoscale) 2. Phase Transformations 3. Microstructure Evolution 4. Computational Thermodynamics/Kinetics 5. Computational Materials Science 6. Design of Experiments and Optimization 7. Materials Informatics

1.6 Personnel

The LSMB has 13 government employees, 10 contract employees, and 3 postdoctoral research associates: Dr Scott Middlemas (PhD, University of Utah, 2013), Dr Shawn Coleman (PhD, University of Arkansas, 2014), and Dr Chad Hornbuckle (PhD, University of Alabama, 2014). In FY14, there were 4 guest researchers within the branch: Dr Mark Atwater (Millersville University), Mr Tyler Cook (Penn State University), Mr Nicholas Krywopusk (Johns Hopkins University), and Mr James Paramore (University of Utah).

Fig. 2 LSMB at the US Army Research Laboratory

The government civilian employees are split between 3 teams within LSMB: 1) Integrity and Sustainability team, 2) Design and Synthesis Team, 3) Strategic Alloys and Applications team. The government civilians are:

- Mr Brady G Butler, materials engineer, BS metallurgical engineering (University of Utah)
- Mr James E Catalano, physical science technician, AS building construction technology, AS welding engineering technology (Wentworth Institute of Technology)
- Mr John F Chinella, materials engineer, BS metallurgical engineering (University of Washington), MS materials science and engineering (Worcester Polytechnic Institute)

- Dr Kris A Darling, materials engineer, BS/PhD materials science and engineering (North Carolina State University)
- Dr Kevin J Doherty, materials engineer, BS metallurgical engineering (Michigan Technological University), PhD materials science and engineering (University of Virginia)
- Mr Scott M Grendahl, materials engineer and Integrity and Sustainability team leader, BS materials science and engineering (Worcester Polytechnic Institute)
- Dr Vince H Hammond, materials engineer, BS materials science & engineering (North Carolina State University), MS engineering mechanics (Virginia Tech), PhD materials science and engineering (University of Virginia)
- Dr Laszlo J Kecskes, materials engineer and Design and Synthesis team leader, BS physics (Rensselaer Polytechnic Institute), MS physics (University of Minnesota), PhD materials science and engineering (University of Delaware)
- Mr Eric M Klier, materials engineer and Strategic Alloys and Applications team leader, BS metallurgical engineering (Illinois Institute of Technology), MS materials science and engineering (Massachusetts Institute of Technology)
- Ms Heidi Maupin, LSMB branch chief, BS metallurgy and metallurgical engineering, ME materials science & engineering (University of Utah)
- Dr Heather A Murdoch, materials engineer, BS materials engineering (Purdue University), PhD materials science and engineering (Massachusetts Institute of Technology)
- Dr Tomoko Sano, materials engineer, BS chemical engineering, MS/PhD materials science and engineering (Carnegie Mellon University)
- Dr Mark A Tschopp, materials engineer, BS/MS metallurgical engineering (Missouri University of Science and Technology), PhD materials science and engineering (Georgia Institute of Technology)

The contract employees in LSMB support both internal mission programs and external customer programs for the US Army. The contract employees include: Dr Bill de Rosset, Mr Sean Fudger, Mr Micah Gallagher, Ms Judy Hays, Mr Hoang Nguyen, Mr Anthony Roberts, Mr David Runk, Ms Larissa Soos, and Mr Kevin Staigerwald.

2. FY14 Research and Development Summary

2.1 LSMB Selected Highlights

Strategic Environmental Research and Development Project (SERDP) Project-of-the-Year Award. In 2014, Mr Scott Grendahl of LSMB was awarded the Weapons Systems and Platforms SERDP 2014 Project-of-the-Year Award for his design-of-experiment evaluation of hydrogen re-embrittlement. Scott Grendahl developed a method that broadens the use of maintenance cleaners and coatings for steel. The result is an estimated savings to the Department of Defense (DOD) of millions of dollars over the next few years alone. Mr Grendahl derived the hydrogen tolerance for steels of varying strengths; for steels with ultimate strengths below 200 ksi, this information proved that particular chemical maintenance procedures are safe without further treatment. This finding is significant to the DOD since over 75% of steels used have ultimate strengths between 140 and 200 ksi. Currently, the DOD requires that parts must undergo a relief heat treatment after maintenance cleaning and/or coating to prevent hydrogen embrittlement from the process. Since hydrogen damage is cumulative, determining the effect from the combined processing of coating and cleaning was crucial to reducing the risk associated with replacing cadmium.

In this SERDP-funded project, Mr Grendahl and his team used the design of experiment approach in 3 phases to investigate the hydrogen re-embrittlement effects of common aviation maintenance chemicals and coatings. Both material and geometry were examined to uncover the best constraints for a novel test method. While traditional testing uses a pass/fail approach, the newly developed method employs load monitoring cells over a range of material strength, hydrogen emitting environment, and applied load, which allowed prospective solvent replacement chemicals and cadmium replacement coatings to be finely delineated in terms of performance. The team also developed a modeling-based tool for predicting time-to-failure under any combination of parameters. The SERDP project team includes:

- Mr Scott Grendahl, US Army Research Laboratory (LSMB)
- Mr Hoang Nguyen, Bowhead Science and Technology LLC (LSMB)
- Dr Shuying Zhu, Dr Stephen P Jones, Mr Ed A Babcock, Dr Joseph H Osborne, Mr Stephen P Gaydos, Boeing Research & Technology
- Mr Chad Hogan, US Air Force
- Mr Richard Green, Green Specialty Service Inc.
- Mr David Kelly, Asko Processing Inc.

LSMB Takes a Leadership Role in the ARL Postdoctoral Association. In 2014, Dr Heather Murdoch cochaired the newly-formed US Army Research Laboratory Postdoctoral Association (ARL-PDA) Media and Public Relations Committee. The ARL-PDA was officially sanctioned in July 2014 to serve the professional, academic, and personal development of postdoctoral researchers, and is the first such organization at a DOD laboratory. Dr Murdoch's efforts directly led to improving the access to and quality of information regarding the postdoctoral appointments and postdoctoral research at ARL, both for current and future postdoctoral research appointments. Her efforts served to help recruit high-quality researchers to the Army, facilitated collaborations, and provided dissemination of tools and information to support current postdoctoral researchers. Dr Murdoch drafted and overhauled the internal and external ARL websites. Dr Murdoch ensured timely support of incoming postdocs, and facilitated connections between postdoctoral researchers and collaborators at ARL and the US Army Research Office (ARO) by building a tool to collect and maintain postdoctoral subject matter experts, mentors, and their research interests. Dr Murdoch directly contributed to the growth of the postdoctoral program at ARL, which is integral to the long-term success of the laboratory.

LSMB Establishes Robust Rare Earth Program. In 2014, Mr Eric Klier envisioned, developed, and established a first-of-its-kind robust program within the Army to identify and resolve the fundamental barriers for heavy rare earth elements: 1) achieving a reliable domestic supply chain for critical heavy rare earth elements, 2) reducing the content of rare earth metals in active material systems, and 3) reducing the materials criticality risk. Mr Klier brought together a broad professional network of subject matter specialists to address this critical endeavor. On November 12, 2014, highlights of the initial results were exchanged at a Nano and Rare Earth Element review meeting at Aberdeen Proving Ground, MD. Mr Klier hosted nearly 60 visitors, which included 10 foreign nationals, whom represented nearly 15 companies and 10 universities, as well as 50 Army civilians to showcase and energize his enterprise. Notably, Mr Klier's direction has already resulted in the operation of the first solvent-extraction pilot plant for heavy rare earth separation within North America in decades and is directly addressing one of the most significant gaps in the re-establishment of a domestic rare earth element supply chain.

LSMB Advances the State of the Art in Materials Science and Engineering. LSMB engages in both fundamental and applied research and development for the

mission of the US Army. This report provides a snapshot of openly-published fundamental research conducted in FY14 by LSMB and with external collaborators, both of which are included in the following subsections and in Appendices A and B. In FY14, LSMB authored or coauthored over 50 refereed journal publications, ARL technical reports, book chapters, and nonrefereed publications; and was the primary presenter or coauthor on over 100 submitted and invited conference presentations; internal and external briefings; and invited university seminars. Additionally, LSMB actively participates in several materials science and engineering related conferences, most notably the professional society conferences Materials Science & Technology (MS&T) 2013 and The Minerals, Metals, and Materials Society (TMS) 2014, where multiple submitted and invited research presentations discuss how LSMB is contributing towards advancing the state of the art in materials science and engineering research.

2.2 Refereed Journal Papers

Peer-reviewed journal publications were published in some of the top materials science, material physics, and material chemistry journals, e.g., Acta Materialia, Materials Science and Engineering A, Physical Review B, Journal of Alloy and Compounds, Intermetallics, JOM, Metallurgical Transactions A, Journal of Applied Physics, Physical Chemistry and Chemical Physics, Computational Materials Science, Journal of Materials Science, Journal of the American Chemical Society, Materials and Design, Materials Research Letters, Advanced Engineering Materials, Journal of Physics: Condensed Matter, and Wear.

The first page of several peer reviewed journal publications for LSMB in FY14 are attached in Appendix A. Here is the complete listing of all FY14 refereed journal publications in LSMB:

1) Asadi E, Zaeem MA, Moitra A, Tschopp MA. Effects of vacancy defects on generalized stacking fault energy of FCC metals. Journal of Physics: Condensed Matter. 2014;26:115404.

2) Atwater MA, Darling KA, Tschopp MA. Towards reaching the theoretical limit of porosity in conventional solid state metal foams: Intraparticle expansion as a primary and additive means to create porosity. Advanced Engineering Materials. 2014;16:190–195.

3) Darling KA, Tschopp MA, Guduru RK, Yin WH, Wei Q, Kecskes LJ. Mi-

crostructure and mechanical properties of bulk nanostructured Cu–Ta alloys consolidated by equal channel angular extrusion. Acta Materialia. 2014;76: 168–185.

4) Darling KA, Tschopp MA, Atwater MA, VanLeeuwen BK, Liu ZK, Mitigating grain growth in binary nanocrystalline alloys through solute selection based on thermodynamic stability maps. Computational Materials Science. 2014;84:255–266.

5) Darling KA, Tschopp MA, Roberts AJ, Armstrong L, Kapoor D, Mathaudhu SN, Kecskes LJ. Influence of Mn solute content on grain size reduction and improved strength in mechanically alloyed Al-Mn alloys. Materials Science and Engineering A. 2014;589:57–65.

6) Darling KA, Roberts AJ, Mishin Y, Mathaudhu SN, Kecskes LJ, Grain size stabilization of nanocrystalline copper at high temperatures by alloying with tantalum. Journal of Alloys and Compounds. 2013;573:142–150.

7) de Rosset WS, Montgomery JS. Cobalt-base alloy gun barrel study. Wear. 2014;316:119–123.

8) El Kadiri H, Barrett CD, Tschopp MA. The candidacy of shuffle and shear during compound twinning in hexagonal close-packed structures. Acta Materialia. 2013;61:7646–7659.

9) Eshraghi M, Tschopp MA, Zaaem MA, Felicelli SD. Effect of resistance spot welding parameters on weld pool properties in a DP600 dual-phase steel: A parametric study using thermomechanically-coupled finite element analysis. Materials and Design. 2014;56:387–397.

10) Fang ZZ, Middlemas S, Guo J, Fan P. A new, energy-efficient chemical pathway for extracting Ti metal from Ti minerals. Journal of the American Chemical Society. 2013;135(49):18248–18251.

11) Hu YJ, Lieser AC, Saengdeejing A, Liu ZK, Kecskes LJ. Glass formability of W-based alloys through thermodynamic modeling: W–Fe–Hf–Pd–Ta and W–Fe–Si–C. Intermetallics. 2014;48:79–85.

12) Kotan H, Darling KA, Saber M, Scattergood RO, Koch CC. Thermal stability and mechanical properties of nanocrystalline Fe–Ni–Zr alloys prepared by mechanical alloying. Journal of Materials Science. 2013;48(24):8402–8411.

13) Liyanage L, Houze J, Kim S, Tschopp MA, Kim SG, Baskes MI, Horstemeyer MF. Structural, elastic and thermal properties of cementite (Fe_3C) calculated using modified embedded atom method. Physical Review B. 2014;89: 094102.

14) Nouranian S, Tschopp MA, Gwaltney SR, Baskes MI, Horstemeyer MF. An interatomic potential for saturated hydrocarbons based on the modified embedded-atom method. Physical Chemistry Chemical Physics. 2014;16: 6233–6249.

15) Rajagopalan M, Bhatia MA, Solanki KN, Tschopp MA, Srolovitz D. Atomic-scale analysis of liquid-gallium embrittlement of aluminum grain boundaries. Acta Materialia. 2014;73:312–325.

16) Rajagopalan M, Tschopp MA, Solanki KN. Grain boundary segregation of interstitial and substitutional impurity atoms in alpha-iron. Journal of Materials. 2014;66:129–138.

17) Roy D, Mahesh BV, Atwater MA, Chan TE, Scattergood RO, Koch CC. Grain size stability and hardness in nanocrystalline Cu–Al–Zr and Cu–Al–Y Alloys. Materials Science and Engineering A. 2014;598:217–223.

18) Shang SL, Wang Y, Du Y, Tschopp MA, Liu ZK. Integrating computational modeling and first-principles calculations to predict the stacking fault energy for dilute multicomponent Ni-base alloys. Computational Materials Science. 2014;91:50–55.

19) Shang SL, Wang WY, Zhou BC, Wang Y, Darling KA, Kecskes LJ, Mathaudhu SN, Liu ZK. Generalized stacking fault energy, ideal strength and twinnability of dilute Mg-based alloys: A first-principles study of shear deformation. Acta Materialia. 2014;67:168–180.

20) Su J, Guo WG, Kecskes LJ, Mathaudhu SN, Wei Q. A rate dependent constitutive model for ECAE Cu based on instrumented nanoindentation results. Materials Science and Engineering A. 2014;597:279–287.

21) Tschopp MA, Gao F, Solanki KN. Binding of He_nV clusters to α-Fe grain boundaries. Journal of Applied Physics. 2014;115:233501.

22) Tschopp MA, Gao F, Yang L, Solanki KN. Binding energetics of substitutional and interstitial helium and di-helium defects with grain boundary struc-

ture in α-Fe. Journal of Applied Physics. 2014;115:033503:1–16.

23) Tschopp MA, Murdoch HA, Kecskes LJ, Darling KA. "Bulk" nanocrystalline metals: Review of the current state of the art and future opportunities for copper and copper alloys. Journal of Materials. 2014;66:1000–1019.

24) Tschopp MA, Miller JD, Oppedal AL, Solanki KN. Characterizing the local primary dendrite arm spacing in directionally-solidified dendritic microstructures. Metallurgical Transactions A. 2014;45(1):426–437.

25) Wang WY, Shang SL, Wang Y, Darling KA, Kecskes LJ, Mathaudhu SN, Hui XD, Liu ZK. Electronic structures of long periodic stacking order structures in Mg: A first-principles study. Journal of Alloys and Compounds. 2014;586:656–662.

26) Wang WY, Shang SL, Wang Y, Mei ZG, Darling KA, Kecskes LJ, Mathaudhu SN, Hui XD, Liu ZK. Effects of alloying elements on stacking faults energies and electronic structures of binary Mg alloys: A first-principles study. Materials Research Letters. 2014;2(1):29–36.

27) Zimmerman J, Sabau A, Zaeem MA, Tschopp MA, Spearot D. Algorithm development in computational materials science. Journal of Materials. 2014;66: 397–398.

2.3 ARL Technical Publications

The cover pages for Distribution A (unclassified, open distribution) ARL Technical Reports, Special Reports, Memorandum Reports, and Reprints for LSMB in FY14 are attached in Appendix B. Here is a list of the FY14 ARL reports:

1) Gusieva K, Birbilis N, Hammond VH, Labukas JP, Placzankis BE. The influence of novel alloying additions on the performance of magnesium alloy AZ31B. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Nov. Report No.: ARL-MR-856.

2) Tschopp MA, Murdoch HA, Kecskes LJ, Darling KA. "Bulk" nanocrystalline metals: Review of the current state of the art and future opportunities for copper and copper alloys. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Jun. Report No.: ARL-RP-485.

3) de Rosset WS, Montgomery, JS. Cobalt-base alloy gun barrel study. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Jul. Report No.: ARL-RP-491.

4) Darling KA, Tschopp MA, Guduru RK, Yin WH, Wei Q, Kecskes LJ. Microstructure and mechanical properties of bulk nanostructured Cu-Ta alloys consolidated by equal channel angular extrusion. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Jul. Report No.: ARL-RP-496.

5) Tschopp MA, Darling KA, VanLeeuwen BK, Atwater MA, Liu ZK. Enhancing the high temperature capability of nanocrystalline alloys: Utilizing thermodynamic stability maps to mitigate grain growth through solute selection. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Dec. Report No.: ARL-TR-6743.

6) Hammond V, Mathaudhu S, Doherty K, Walsh S, Vargas L, Placzankis B, Labukas J, Pepi M, Trexler M, Barnett B, Jones T, Kecskes LJ. Ultrahigh-strength magnesium alloys for the future force: A final report on the 5-year mission program, 2009-2013. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Jan. Report No.: ARL-TR-6788.

7) Hammond VH, Sano T, Labukas JP, Dillon TA, Butler BG, Shen J, Wei Q. Evaluation of an Al, La modified $MgZn_2Y_2$ alloy. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Feb. Report No.: ARL-TR-6807.

8) Grendahl SM, Kellogg F, Nguyen H. Effect of cleanliness on hydrogen tolerance in high-strength steel. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Apr. Report No.: ARL-TR-6885.

9) Kecskes LJ, Plunkett KF. Reactivity of aluminum-based mixtures with early transition metals. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Aug. Report No.: ARL-TR-7027.

10) Tschopp MA, Darling KA. Towards predictive models of nanocrystalline binary metal alloys: Role of solutes and interfaces on segregation and mechanics in Al-based nanocrystalline systems (ISN Year 1 Report). Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Jul. Report No.: ARL-SR-291. (Distribution D)

11) Hammond V, Jones T, Kecskes L, Mathaudhu S, Segal V. Fabrication of high strength AA5083 for armor and structural applications through large scale ECAE processing. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Feb. Report No.: ARL-TR-6815. (Distribution B)

12) Gabriel B, Pepi M, Grendahl S, Wolfe D, Potter J, Eden T. Ultrasonic shot peening as a field deployable alternative to conventional shot peening. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Mar. Report No.: ARL-TR-6868. (Distribution B)

13) Grendahl SM, Snoha DJ, Fudger SJ, Kellogg F, Nguyen H, Runk D. Ultrasonic shot peening for aviation components. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Nov. Report No.: ARL-TR-6740. (Distribution D)

14) Chinella JF. Protection comparisons of aluminum 7020-T651 and 5083-H131. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Sep. Report No.: ARL-TR-6574. (Distribution E)

15) Chinella JF. Protection statistics and performance of aluminum 7020-T651. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Nov. Report No.: ARL-TR-6727. (Distribution E)

16) Doherty KJ, Thompson B, Eff M. Friction stir processing of the high-strength aluminum alloy 2139-T8 to eliminate spall. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Mar. Report No.: ARL-TR-6864. (Distribution C)

17) Montgomery JS. Unified taxonomy of aircraft armor protection. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Sep. Report No.: ARL-TR-6683. (Distribution D)

18) de Rosset WS. Gun tube liners – A historical perspective. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2014 Mar. Report No.: ARL-CR-733. (Distribution B)

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Appendix A. FY14 Journal Publications

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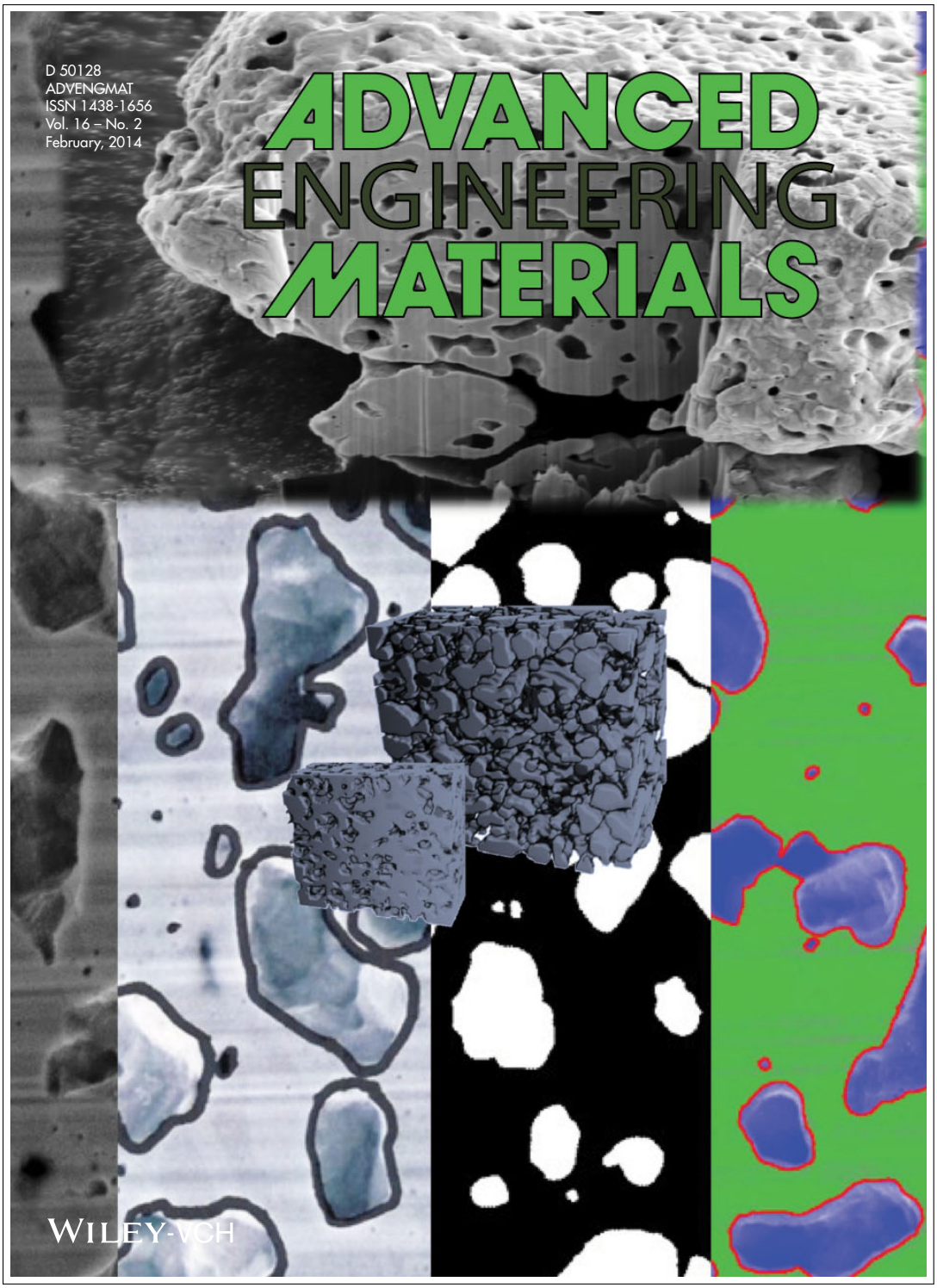

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Effect of vacancy defects on generalized stacking fault energy of fcc metals

Ebrahim Asadi[1], **Mohsen Asle Zaeem**[1], **Amitava Moitra**[2] **and Mark A Tschopp**[3,4]

[1] Materials Science and Engineering Department, Missouri University of Science and Technology, Rolla, MO 65409, USA
[2] S N Bose National Centre for Basic Sciences, Kolkata, India
[3] Engility Corporation at the US Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA
[4] Center for Advanced Vehicular Systems, Mississippi State University, Starkville, MS 39759, USA

E-mail: AsadiE@mst.edu and Zaeem@mst.edu

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Abstract
Molecular dynamics (MD) and density functional theory (DFT) studies were performed to investigate the influence of vacancy defects on generalized stacking fault (GSF) energy of fcc metals. MEAM and EAM potentials were used for MD simulations, and DFT calculations were performed to test the accuracy of different common parameter sets for MEAM and EAM potentials in predicting GSF with different fractions of vacancy defects. Vacancy defects were placed at the stacking fault plane or at nearby atomic layers. The effect of vacancy defects at the stacking fault plane and the plane directly underneath of it was dominant compared to the effect of vacancies at other adjacent planes. The effects of vacancy fraction, the distance between vacancies, and lateral relaxation of atoms on the GSF curves with vacancy defects were investigated. A very similar variation of normalized SFEs with respect to vacancy fractions were observed for Ni and Cu. MEAM potentials qualitatively captured the effect of vacancies on GSF.

Keywords: generalized stacking fault, vacancy, DFT, EAM, MEAM, molecular dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

Despite the fact that even brittle materials at small deformation have an infinitesimally plastic behavior, most continuum models assume that the material is either brittle or ductile, predicting two different deformation behaviors and failure mechanisms for these two types of materials. Therefore, the ability to determine the ductility of the material via a reliable criterion is important to capture when modeling materials at continuum scales. Such a criterion to quantify ductility may be defined based on the energy required to nucleate dislocations, such as those proposed in [1–3], which require two material parameters: the unstable stacking fault energy γ_{us} and intrinsic (or stable) stacking fault energy γ_{sf}. Generalized stacking fault energies are calculated by displacing atoms above a fault plane by a displacement vector while holding atoms below the fault plane fixed [4]. The required energy per unit area to displace these atoms plotted against displaced distance is called generalized stacking fault (GSF) [5], which is typically a sinusoidal graph for most metals. As the displacement distance increases, the crystal configuration reaches an unstable position whereby the required energy per unit area, or stacking fault energy (SFE), is at a maximum value (γ_{us}). This is the energy barrier that must be overcome to nucleate a dislocation. Further displacement allows the lattice structure to reach a stable configuration with a SFE of γ_{sf}. Since only the stable SFE (γ_{sf}) of the GSF curve can be measured experimentally, there have been a number of efforts to calculate this curve through modeling and simulating methods such as molecular dynamics (MD) and density functional theory (DFT). However, many of

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Towards Reaching the Theoretical Limit of Porosity in Solid State Metal Foams: Intraparticle Expansion as A Primary and Additive Means to Create Porosity**

By *Mark A. Atwater,* Kris A. Darling* and *Mark A. Tschopp*

Metallic foams and porous metal structures are valuable for their unique characteristics such as high specific strength, energy absorption at constant crushing load, efficient heat transfer and acoustic properties, all of which can be tailored by controlling the porosity.[1–3] Many techniques for generating metal foams exist, but the vast majority of metal foam production is through liquid state processes such as the melt processing of aluminum by gas injection or decomposition of a dispersed foaming agent.[4] Aluminum has dominated the metal foam industry due to its low melting temperature and relative stability in air.[5] Reactive metals and those with higher melting temperatures require special processing, usually through solid state techniques.[3,6–11] The solid state foaming of metals by gas entrapment[12,13] typically uses a two-step process: (i) entrap gas within the interparticle voids during powder consolidation and (ii) heat to expand the entrapped gas such that the internal pressure exceeds the yield strength and enables plasticity or creep to increase porosity.[14] While some powder metallurgy (PM) processes can exceed 85% porosity (e.g. using a polymer foam as a fugitive template [7]), it is more common for PM processes to produce porosity levels between 20 and 40%.[5,14] In fact, Elzey and Wadley[14] calculated that the limit of the solid state foaming process by gas entrapment is ≈65% porosity, even under ideal, superplastic conditions. Experimentally, this method has produced foams with porosity only as high as 53%,[15] but porosity has typically been limited to ≈40%. These relatively low porosity levels (compared to liquid state processes) constrain the applications of metal foams produced via solid state foaming. To extend the capabilities of solid state foaming, we have developed an additive means of creating porosity by intraparticle expansion.

[*] *M. A. Atwater, K. A. Darling, M. A. Tschopp*
US Army Research Laboratory, Weapons and Materials Research Directorate, Lightweight and Specialty Metals Branch, Aberdeen Proving Ground, MD 21005, USA
E-mail: mark.atwater@millersville.edu
M. A. Atwater
Department of Applied Engineering, Safety and Technology, Millersville University, Millersville, PA 17551, USA

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The current limitation of solid-state expansion by gas entrapment is dictated by voids formed between *solid* particles during consolidation. In this model, the initial gas pressure and foaming temperature determine the resulting porosity. However, if the expanding gas is not limited to just that which is trapped between particles, but is also located *within* particles, solid state foaming may assume a character more akin to expandable polymers which foam from the constituent pellets. This concept is a paradigm shift in terms of the solid state foaming process and the achievable levels of porosity. On the basis of this simple, powder feedstock expansion, there is universal application to powder metallurgy methods for foaming. In this work, we examine the microstructure and morphology of a Cu–Sb alloy that expands to porosities of close to 40% *within* individual particles, resulting in absolute porosity of 69% in sintered samples.

The Cu–Sb alloy powder was formed by mechanically alloying Cu and Sb (Alfa Aesar, 99.9 and 99.5%, respectively) at cryogenic temperature (−196 °C) for 4 h using a modified SPEX 8000M Mixer/Mill. The elemental powders were combined to achieve 5 at% Sb in Cu. The as-milled powders contained no appreciable porosity. Ball milling was used as a means to intimately mix the elements and refine and distribute pre-existing oxides. Although oxygen exposure was controlled during milling and storage of powders, the manufacturer-supplied precursors did contain appreciable oxygen content. The importance of this will be detailed later. The alloyed powder was annealed at 600 °C for a period of 1 h under 3% H_2 (bal. Ar). During annealing, the powders underwent pore formation and expansion. When annealing was done in the absence of H_2, it did not produce any expansion. Microscopic examination of the loose powders was carried out using an FEI Nova Nano Lab 600 dual beam microscope using scanning electron microscopy (SEM). Cross-sectional analysis was performed using a focused ion beam (FIB). The grain size and grain orientations were measured using focused ion beam ion channeling contrast imaging (FIBICC) and electron backscatter diffraction (EBSD), respectively. FIB serial sectioning of the individual powder particles was used to visualize and quantify a representative three-dimensional (3D) pore structure in a volume 25.6 μm wide, 22.1 μm high, and 12.5 μm deep. For bulk measurement, the as-milled powders were also compacted in a die with a circular cross-section 3 mm in

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Grain size stabilization of nanocrystalline copper at high temperatures by alloying with tantalum

K.A. Darling [a,*], A.J. Roberts [b], Y. Mishin [c], S.N. Mathaudhu [d], L.J. Kecskes [a]

[a] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005-5069, USA
[b] ORISE Program, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069, USA
[c] George Mason University, Dept of Physics and Astronomy, Fairfax, VA 22030, USA
[d] U.S. Army Research Laboratory, Army Research Office, Research Triangle Park, NC 27709-2211, USA

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ABSTRACT

Nanocrystalline Cu–Ta alloys belong to an emerging class of immiscible materials with potential for high-temperature applications. Differential scanning calorimetry (DSC), Vickers microhardness, transmission and scanning electron microscopy (TEM/SEM), and atomistic simulations have been applied to study the structural evolution in high-energy cryogenically alloyed nanocrystalline Cu–10 at.%Ta. The thermally induced coarsening of the as-milled microstructure was investigated and it was found that the onset of grain growth occurs at temperatures higher than that for pure nanocrystalline Cu. The total heat release associated with grain growth was 0.553 kJ/mol. Interestingly, nanocrystalline Cu–10 at.%Ta maintains a mean grain size (GS) of 167 nm after annealing at 97% of its melting point. The increased microstructural stability is attributed to a combination of thermodynamic and kinetic stabilization effects which, in turn, appear to be controlled by segregation and diffusion of Ta solute atoms along grain boundaries (GBs). The as-milled nanocrystalline Cu–10 at.%Ta exhibits Vickers microhardness values near 5 GPa surpassing the microhardness of conventional pure nanocrystalline Cu by ~2.5 GPa.

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1. Introduction

The coarsening and grain growth of nanocrystalline metals produced by high energy mechanical alloying has been the focus of intense research efforts over the past 30 years. A large fraction of the studies report observations and/or methods which limit or reduce grain growth in these materials. Such reports have spawned an area of research that focuses on preventing grain growth in nanocrystalline materials. Currently, there are two predominant methods for preventing the grain growth: a kinetic approach and a thermodynamic approach. The kinetic approach invokes a pinning force to trap grain boundaries (GBs) in place thereby halting grain growth [1,2]. This can be accomplished in a number of ways, the most prominent being the pinning with secondary phases [3–6] and/or the solute drag-effects [7,8]. In contrast, the thermodynamic approach, recently proposed theoretically, is associated with suppressing the driving force for grain growth by reduction of the GB free energy [9–16]. The most successful thermodynamic approaches have relied on the use of GB stabilizing solute atoms for reducing the free energy penalty (lower GB free energy) associated with the presence of excess GBs [17–23]. To a lesser extent, GB engineering has also been utilized to produce microstructures composed of low energy nanotwinned boundaries, thereby stabilizing the overall microstructure [24,25]. Recently, Atwater and Darling have published a visual library outlining the thermodynamic stability of 2288 distinct binary nanocrystalline systems [26]. Currently, interest has been growing to investigate the combined effect of both kinetic and thermodynamic mechanisms of stabilization operating in the same systems [27–30].

Despite the depth and versatility of this growing area of research, nanocrystalline metals exhibiting microstructural stability at extreme temperatures continue to remain an extraordinary scientific curiosity. To the knowledge of the authors, there are only a few existing examples that experimentally demonstrate the retention of nanocrystallinity at high homologous temperatures (i.e., >80% of the melting point, T_m) [31–33]. Botcharova et al. [31] reported on a nanocrystalline Cu–Nb alloy prepared by high-energy mechanical alloying, whose microstructure remained nanocrystalline up to temperatures near T_m of the alloy. More recently, atomistic simulations of a similar alloy system were reported, revealing an extremely high microstructural stability of nanocrystalline Cu alloyed with Ta [34]. Both of these alloys are unique as they represent systems that have the potential to exhibit both highly effective thermodynamic and kinetic modes of stability. Specifically, in Cu–Ta, thermodynamic parameters such as the +2 kJ/mol equimolar enthalpy of mixing, the 43.6 kJ/mol elastic enthalpy [35,36] and a 0% solubility limit strongly suggest that if forced

* Corresponding author.
E-mail address: kristopher.darling.civ@mail.mil (K.A. Darling).

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Microstructure and mechanical properties of bulk nanostructured Cu–Ta alloys consolidated by equal channel angular extrusion

K.A. Darling [a,*], M.A. Tschopp [a], R.K. Guduru [b], W.H. Yin [c], Q. Wei [c], L.J. Kecskes [a]

[a] US Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005, USA
[b] Department of Mechanical Engineering, University of Michigan, Dearborn, MI 48128, USA
[c] Department of Mechanical Engineering and Engineering Science, University of North Carolina at Charlotte, Charlotte, NC 28223, USA

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Abstract

Nanostructured Cu–Ta alloys have shown promise as high-strength nanocrystalline materials in part due to their limited grain growth at high temperatures. In the present study, Cu–Ta alloy powders, synthesized via high-energy cryogenic mechanical alloying, were consolidated into bulk nanostructured specimens using equal channel angular extrusion (ECAE) at high temperatures. Subsequent microstructure characterization indicated full consolidation, which resulted in an equiaxed grain structure for the Cu matrix along with the formation of fine Ta precipitates, the size distributions of which varied both with composition and processing temperature. Microhardness, compression and shear punch testing indicated, in some cases, an almost threefold increase in mechanical properties above that predicted by Hall–Petch estimates for pure nanocrystalline Cu. Stress relaxation tests substantiated the strain-hardening behavior and grain-size-dependent dislocation activity observed in the nanocrystalline Cu–Ta samples.
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Keywords: Nanocrystalline alloys; Cu–Ta alloys; Equal channel angular pressing; Mechanical behavior; Dynamic compression test

1. Introduction

Nanocrystalline and nanostructured materials have spawned significant interest due to the unique set of properties unachievable by coarse-grained polycrystalline materials. However, synthesis and consolidation of these nanostructured materials into bulk parts is often very challenging, attributed in part to limitations in processing methods that are not easily scalable (e.g. electrodeposition, vapor deposition) or due to uncontrolled grain growth of the non-equilibrium structure during processing. The synthesis of novel nanostructured alloys formed from forced solid solutions between elemental Cu and immiscible solute species has been the focus of several recent studies [1–7]. These non-equilibrium solid solutions have been shown to evolve and form well-dispersed nanoscale composite alloys upon annealing at elevated temperatures. In some cases, the coarsening mechanism observed after phase separation in such alloys has been attributed to the segregation and diffusion of the immiscible solute species along grain boundaries [2,5]. While both simulations and experiments indicate remarkable physical properties for this new class of materials [1,5,8,9], to date only small-scale testing methods (e.g. microhardness measurements) have been used to probe the deformation mechanisms due to limitations in producing bulk test specimens. It is well known that there are often size effects in mechanical properties (e.g. micropillar compression [10]), hence further work with bulk consolidated nanostructured Cu alloys can help to accurately assess the representative mechanical properties and behavior of bulk parts.

* Corresponding author.
E-mail address: kristopher.darling.civ@mail.mil (K.A. Darling).

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Mitigating grain growth in binary nanocrystalline alloys through solute selection based on thermodynamic stability maps

K.A. Darling [a,*], M.A. Tschopp [a,*], B.K. VanLeeuwen [b], M.A. Atwater [c], Z.K. Liu [b]

[a] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005, USA
[b] Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA
[c] Applied Engineering, Safety & Technology Department, Millersville University, Millersville, PA 17551, USA

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ABSTRACT

Mitigating grain growth at high temperatures in binary nanocrystalline alloys is important for processing nanocrystalline alloy systems. The objective of this research is to develop a methodical design-based approach for selecting solutes in binary nanocrystalline alloys by revisiting grain boundary thermodynamics and the internal processes of grain growth and solute segregation in a closed system. In this work, the grain boundary energy is derived and systematically studied in terms of temperature, grain size, concentration, and solute segregation for binary systems of 44 solvents and 52 solutes, using readily-available elemental data, such as moduli and liquid enthalpy of mixing. It is shown that through solute segregation, the grain boundary energies of some binary systems can be reduced, resulting in thermodynamically stable grain structures and successful prediction of solutes that inhibit grain growth in some nanocrystalline alloys. Parametric studies reveal trends between equilibrium grain size, solute distribution and temperature for various binary systems culminating in the generation of nanocrystalline thermodynamic stability maps as a tool for solute selection in binary nanocrystalline alloys.

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1. Introduction

Nanocrystalline (nc) alloys [1] are an important subset of metallic materials due to their small grain size (<100 nm) which imparts properties and potential applications that may not be achievable using conventional coarse-grained polycrystalline materials. For instance, they tend to possess extremely high strengths [2–8] that are associated with grain boundary strengthening (*i.e.*, the Hall–Petch effect [9,10]). A fundamental limitation to their use comes from their inherent thermal instability, which has been extensively explored using both experiments [11–19] and computational approaches [20–33]. The small grain size produces an extremely large driving force for grain growth. If not kept in check, grain growth can occur at modest temperatures, even at room temperature in pure materials such as copper and palladium [34]. Since bulk nanocrystalline alloys are often produced via mechanical alloying [35,36], this grain growth phenomenon provides a significant obstacle to consolidating the nanocrystalline powders by traditional powder metallurgy techniques where high temperature sintering is common.

There are several methods that have been devised to circumvent this temperature sensitivity and stabilize the grain size. Grain size stabilization commonly involves adding small quantities of an insoluble element (*i.e.*, solute). Nonequilibrium processing (*e.g.*, mechanical alloying, rapid solidification, etc.) is often used to force the solute into solution and, upon heating, the solute segregates to interfaces such as grain boundaries [37,38]. Alternatively, the solute will remain in solution or precipitate out as a second phase. These two basic mechanisms for stabilization are known as thermodynamic and kinetic stabilization, respectively [39]. For kinetic stabilization, the solute acts to hinder grain boundary mobility by diffusion-related means such as solute drag [40] or by pinning boundaries with a fine dispersion of precipitates [41]. For thermodynamic stabilization, solute is expected to segregate to grain boundaries and reduce the grain boundary energy so as to minimize or eliminate the driving force for grain growth [16,20,32,42–49]. Since grain boundary energy is the driving force for grain growth, a reduction in grain boundary energy can impede or even entirely inhibit grain growth. The reduction in grain boundary energy provided by a segregating solute is determined by the segregation energy, ΔG_{seg} [16,20,32,42–49]. Since the values of ΔG_{seg} are usually not available, they are estimated. Wynblatt and Chatain [50] recently reviewed the analytical models on segregation to grain boundaries (GBs) and surfaces and addressed the difficulty of meaningful definitions of segregation enthalpy, entropy, and free energy among various issues. The central equation for all models is as follows for a binary system:

* Corresponding authors.
E-mail addresses: kristopher.darling.civ@mail.mil (K.A. Darling), mark.tschopp@gatech.edu (M.A. Tschopp).

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Influence of Mn solute content on grain size reduction and improved strength in mechanically alloyed Al–Mn alloys

K.A. Darling [a,*], A.J. Roberts [a], L. Armstrong [b], D. Kapoor [b], M.A. Tschopp [a], L.J. Kecskes [a], S.N. Mathaudhu [c]

[a] U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA
[b] U.S. Army RDECOM-ARDEC, Picatinny Arsenal, NJ, USA
[c] U.S. Army Research Office, Research Triangle Park, NC, USA

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ABSTRACT

Al–Mn alloys with a solid-solution Mn content ranging from 0 to 3.1 at% were successfully prepared by high energy mechanical alloying at room temperature of an Al–8 at% Mn sample. The solubility level obtained is up to five times the equilibrium solubility limit of Mn in Al (from 0.62 at% Mn). In general, the observed microstructures are consistent with being a nanocomposite composed of an Al–Mn solid solution matrix with dispersed Mn particles. For alloys with solid solutions up to 3.1 at%, increasing the Mn content correlated with a decrease in the matrix grain size down to a minimum of 12 nm. High hardness values of ~4 GPa were obtained. The main strengthening mechanism of the Al–Mn alloys is attributed to the grain size reduction. Further attempts to increase the dissolved solute content resulted in the precipitation of the Al_6Mn equilibrium intermetallic phase.

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1. Introduction

Aluminum alloys have a broad range of lightweight structural applications due to their combination of density, tensile strength, and ductility. Hence, there has been significant interest in nanocrystalline aluminum alloys [1–16] in order to further increase their strength through grain size reduction (i.e., Hall–Petch strengthening). The additions of secondary elements such as Fe [6–9], Zr [12,13], W [10], Mg [11], and Mn [3,4], to name a few, have helped to increase the strength of these alloys, while also contributing to increased thermal stability, in some cases [1]. Nanocrystalline Al–Mn alloys recently produced by Ruan and Schuh using an electrodeposition process have demonstrated both a nanocrystalline grain size <100 nm and hardness values up to 5 GPa (corresponding to a tensile strength that exceeds 1.5 GPa) [4]. The source of these remarkable properties is suspected to be the combination of unique microstructures (microcrystalline, nanocrystalline, amorphous and nano-quasicrystalline structures [3,4], all of which were found to be inherently linked to the overall dissolved Mn content (0–8 at%). Similar results were previously reported by Inoue through melt spinning Al–Mn–Ce alloys which demonstrated both high tensile fracture strengths (1.3 GPa) and good ductility [17]. Microstructural features, similar to those reported by Ruan and Schuh, were also reported, i.e., a fine distribution of quasicrystalline particles in an Al-rich solid solution matrix with an additional amorphous phase. Inoue et al. suggest that the interfacial bonding between the particle and matrix phases are enhanced by the existence of a crystalline approximate phase. This scenario may result in a continuous load transfer from the soft ductile Al-rich matrix to the high strength quasicrystalline phase leading to the enhanced ductility observed in these alloys.

The electrodeposition and melt spinning processes are not able to efficiently scale these microstructures to produce bulk nanostructured materials for structural engineering applications. Given the encouraging results reported by Ruan [3,4] and Inoue [17], the ability to scale these Al–Mn alloys to applications that demand high strengths and good bending ductility is certainly of interest. This prior work provides the motivation for investigating the feasibility of fabricating these Al–Mn binary alloys with high energy powder metallurgy and consolidation approaches, wherein scalability is less of an issue. High energy mechanical alloying is a well established process for generating nanocrystalline alloys and nanocomposites [18–20]. Similar to electrodeposition and melt spinning, high-energy mechanical alloying is a far-from-equilibrium processing method, capable of dramatically maintaining or increasing solid solubility of one metal in another, well above its equilibrium values [18]. Additionally, unlike both electrodeposition and melt spinning, high-energy mechanical alloying is readily scalable and cost effective, making it a considerably more suitable method of production for these types of alloys. Moreover,

* Corresponding author. Tel.: +1 410 306 0862; fax: +1 410 306 0806.
E-mail address: kristopher.darling.civ@mail.mil (K.A. Darling).

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Cobalt-base alloy gun barrel study

William S. de Rosset*, Jonathan S. Montgomery

U.S. Army Research Laboratory, ATTN: RDRL-WMM-F, Aberdeen Proving Ground, MA 21005, USA

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ABSTRACT

Firing tests of a small caliber experimental gun barrel made of a cobalt-base alloy have been conducted with the purpose of determining the degree of wear and erosion due to excessive firing durations. The small amount of barrel material loss makes the cobalt-base alloy an excellent candidate for use as a gun liner. An unusual wear pattern resulting from this loss was observed near the muzzle. Elimination of chemical and thermal effects made a plausible explanation of the wear pattern possible.

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1. Introduction

For over 50 years, the United States Army has used a short cobalt-chromium liner (Stellite 21®[1]) in its M2 machine gun to reduce barrel wear and erosion. Even though this approach is highly successful, it has not been adopted for use in other fielded weapons. This may be due to the problems faced with emplacing the liner in the barrel or the perceived cost/benefit of the approach. Alternatively, chromium coatings have also proven to be effective in reducing wear. However, the plating process used to apply the chromium to the bore of the tube involves hexavalent chromium, a known carcinogen. This has led to efforts to find ways to replace the chromium plating process.

Recently, advances have been made in explosive bonding of liners to gun tubes [1–3] and in using a pressurization technique to attach the liner [4,5]. This has prompted considerable interest in alternate materials that might be used as liners. The United States Army Research Laboratory (ARL) was able to obtain several 5.56 mm barrels made entirely from a cobalt-chromium alloy. These experimental barrels served as a test bed to determine how this particular alloy would wear under extreme firing conditions. The intent of the firing tests was to demonstrate that a gun tube liner made of this material would extend the service life of the gun tube to the extent that the soldier would not have to carry a second barrel, as is now the case. The next section presents the rationale and procedures for the firing tests as well as the equipment used to measure the bore diameter. The results section gives the experimental findings in terms of barrel wear as a function of shot number. An unusual wear pattern was observed, and this is discussed in the section following the results. Conclusions are presented in Section 5.

2. Materials and methods

The composition of the cobalt-base alloy (CBA) is presented in Table 1. The production of this alloy does not involve the use of hexavalent chromium. Consequently, the use of a liner made of this material would avoid that particular environmental issue.

Careful consideration was given to the firing cadence. In order to demonstrate the wear resistance of the CBA barrel, the plan was to test the barrels at increasing levels of firing durations. The baseline firing rate was that specified by the field manual appropriate for small caliber weapons [6]. The manual specifies two cadences: sustained and rapid. For sustained rate of fire, the manual calls for 3–5 round bursts, with 4–5 s between bursts. The barrel is changed every ten minutes. For rapid fire, the manual calls for 8–10 round bursts with 2–3 s between bursts, and the barrel must be changed every two minutes. The baseline cadence was denoted as the Phase 1 test. Thereafter, the firing tests were conducted with increasing durations. A separate barrel was used for each cadence. Barrel 1 was used for the sustained cadence, and Barrel 2 was used for the rapid cadence. Table 2 presents the complete firing sequence.

* Corresponding author. Tel.: +1 410 306 0816.
E-mail address: william.s.derosset.ctr@mail.mil (W.S. de Rosset).

[1] Stellite 21 is a registered trademark of Kennametal Stellite, Goshen, IN.

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The candidacy of shuffle and shear during compound twinning in hexagonal close-packed structures

Haitham El Kadiri [a,b,*], Christopher D. Barrett [a,b], Mark A. Tschopp [b,c]

[a] Department of Mechanical Engineering, Mississippi State University, Mississippi State, MS 39762, USA
[b] Center for Advanced Vehicular Systems, Mississippi State University, 200 Research Boulevard, MS 39759, USA
[c] Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005, USA

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Abstract

This paper proposes a systematic generalized formulation for calculating both atomic shuffling and shear candidates for a given compound twinning mode in hexagonal closed-packed metals. Although shuffles play an important role in the mobility of twinning dislocations in non-symmorphic crystals, their analytical expressions have not been previously derived. The method is illustrated for both flat planes and corrugated planes which are exemplified by $\{11\bar{2}2\}$ and $\{10\bar{1}2\}$ twinning modes, respectively. The method distinguishes between shuffle displacements and net shuffles. While shuffle displacements correspond to movements between ideal atom positions in the parent and twin lattices, net shuffles comprise contributions from shear on overlying planes which can operate along opposite directions to those of shuffle displacements. Thus, net shuffles in the twinning direction can vanish in a limiting case, as is interestingly the case for those needed in the second plane by the $\mathbf{b_4}$ dislocation candidate in $\{11\bar{2}2\}$ twinning. It is found that while shuffle displacement vectors can be irrational when K_1 is corrugated, net shuffle vectors are always rational.
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Keywords: Crystallography; Shear; Shuffle; Hexagonal; Twinning; Slip

1. Introduction

Recent intense consideration of magnesium and titanium by the automotive and aerospace industries as the best metallic lightweight candidates for massive weight reductions have invigorated investigation of the anisotropy and asymmetry of hexagonal close-packed (hcp) structures. These anisotropy and asymmetry issues are mainly caused by the inability of any close-packed shear deformation mode to provide $\langle c\rangle$-axis deformation. Thus, in the absence of any observed highly glissile pyramidal slip mode, a more difficult non-basal slip direction is required to provide the minimum of five independent slip systems required for arbitrary deformation. The most widely accepted dislocation in the literature possessing a non-zero $\langle c\rangle$ component operates on the second-order pyramidal plane $\{11\bar{2}2\}$ with a net Burgers vector equal to $\frac{1}{3}\langle 11\bar{2}\bar{3}\rangle(\langle c+a\rangle)$ [1–4]. However, the critical resolved shear stress (CRSS) of this dislocation at low temperatures turned out to be higher than that of twinning on any of the pyramidal planes. Hence, various twin modes activate to accommodate either compression or tension of the $\langle c\rangle$ axis. Twinning has been correlated with early crack nucleation, and there is a consensus in the literature that it reduces the ductility of Mg at low temperatures. This limited ductility is currently the main barrier to broader application of Mg in vehicles [5–10]. Because of the diffusional nature of shuffles, some authors "tacitly" proposed that appropriate additions of impurities may be effective in hindering shuffles and, thus, reducing the propensity to twinning [11–13]. Furthermore, shuffles have also been found to play a critical role in the

* Corresponding author at: Department of Mechanical Engineering, Mississippi State University, Mississippi State, MS 39762, USA.
E-mail address: elkadiri@me.msstate.edu (H. El Kadiri).

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Technical Report

Effect of resistance spot welding parameters on weld pool properties in a DP600 dual-phase steel: A parametric study using thermomechanically-coupled finite element analysis

Mohsen Eshraghi [a,b,*], Mark A. Tschopp [a,c], Mohsen Asle Zaeem [d], Sergio D. Felicelli [a,b]

[a] Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, MS 39762, United States
[b] Mechanical Engineering Department, Mississippi State University, Mississippi State, MS 39762, United States
[c] Army Research Laboratory, Materials and Manufacturing Science Division, Lightweight and Specialty Metals Branch, Aberdeen Proving Ground, MD 21005, United States
[d] Department of Material Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409, United States

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ABSTRACT

The objective of this research is to quantify the effects of resistance spot welding (RSW) parameters on different weld properties of a dual-phase steel. A finite element based model was used which accounted for the following required physical interactions: the interaction between (1) the electro-kinetics and heat transfer via the Joule effect, (2) the heat transfer and phase transformations through latent heat, and (3) the heat transfer, electro-kinetics, and mechanical behavior via the contact conditions. The effects of the RSW parameters on weld properties were investigated within a design of experiments framework by altering (1) the electrical current intensity, (2) the welding time, (3) the sheet thickness, (3) the electrode face radius, and (5) the squeeze force at multiple levels. The simulation results were analyzed using the analysis of variance (ANOVA) technique to show the effects of these parameters and their potential interactions, along with their significance. The current intensity was the most influential factor and resulted in an increased size of molten zone and the heat affected zone. The sheet thickness and welding time also showed significant contributions in changing the weld properties. The effects of the other parameters were less significant. The importance of this study is that finding the optimal process window for RSW parameters can help to engineer the desired weld properties.

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1. Introduction

Resistance spot welding (RSW) is the primary welding process for sheet metal and has been predominantly used in the automotive industry, where it serves as a highly productive, low cost, reliable alternative to other welding methods [1]. RSW is accomplished by passing an electrical current through coincident sheets via electrodes. The heat induced by the electrical current creates a molten nugget. The molten nugget grows until the electrical current ceases, at which point the nugget solidifies to create a bond between the sheets [2]. The weld quality is affected by several factors: the intensity of the electrical current, the amount of force applied by the electrodes to the sheets, the thickness and material of the sheets, length of time the pressure and current are applied, the size of electrodes, etc.

RSW has been studied both experimentally and numerically to improve the quality of the produced welds. Experimental studies on nugget formation provide valuable information about the influence of different parameters on the weld properties. In a recent set of studies, Florea et al. [3–5] investigated the influence of nugget formation, failure loads and deformation, and welding parameters on fatigue life and microstructure in RSW of 6061-T6 aluminum alloy; they also determined the residual stresses in RSW by using neutron diffraction measurements [4]. Because of the recent increase in usage of advanced high strength steels (AHSS) such as dual-phase (DP) steels in manufacturing low weight vehicles with improved crash performance, there have been several experimental studies on the RSW of steel sheets [6–12]. Aslanlar et al. [11] investigated the effects of welding time on the tensile-peel strength and tensile-shear strength of welding joints in RSW of chromate micro-alloyed steel sheets. Rogeon et al. [12] studied the RSW of non-alloyed steels (XSG and XES steel sheet) and DP600 dual phase steel sheets and measured the electrical contact resistances allowing for high pressure and temperature; they characterized the contact conditions at the electrode–sheet and sheet–sheet interfaces, which constitute essential variables in the control of the RSW process.

Despite providing practical information, experimental studies on RSW are very costly [13,14]. Numerical studies can help reduce

* Corresponding author. Current address: Department of Mechanical Engineering, Auburn Science and Engineering Center (ASEC) 101, The University of Akron, Akron, OH 44325-3903. Tel.: +1 330 972 3933; fax: +1 330 972 6027.
E-mail address: eshraghi@uakron.edu (M. Eshraghi).

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A New, Energy-Efficient Chemical Pathway for Extracting Ti Metal from Ti Minerals

Zhigang Zak Fang,* Scott Middlemas,† Jun Guo, and Peng Fan

Metallurgical Engineering, University of Utah, Salt Lake City, Utah 84112, United States

Supporting Information

ABSTRACT: Titanium is the ninth most abundant element, fourth among common metals, in the Earth's crust. Apart from some high-value applications in, e.g., the aerospace, biomedicine, and defense industries, the use of titanium in industrial or civilian applications has been extremely limited because of its high embodied energy and high cost. However, employing titanium would significantly reduce energy consumption of mechanical systems such as civilian transportation vehicles, which would have a profound impact on the sustainability of a global economy and the society of the future. The root cause of the high cost of titanium is its very strong affinity for oxygen. Conventional methods for Ti extraction involve several energy-intensive processes, including upgrading ilmenite ore to Ti-slag and then to synthetic rutile, high-temperature carbo-chlorination to produce $TiCl_4$, and batch reduction of $TiCl_4$ using Mg or Na (Kroll or Hunter process). This Communication describes a novel chemical pathway for extracting titanium metal from the upgraded titanium minerals (Ti-slag) with 60% less energy consumption than conventional methods. The new method involves direct reduction of Ti-slag using magnesium hydride, forming titanium hydride, which is subsequently purified by a series of chemical leaching steps. By directly reducing Ti-slag in the first step, Ti is chemically separated from impurities without using high-temperature processes.

Titanium is the ninth most abundant element, fourth among common metals, in the Earth's crust. It has been used as a high-performance light metal in aerospace, defense, biomedical, petrochemical, and other high-value applications owing to its high specific strength, extreme corrosion resistance, and biocompatibility. However, the use of titanium in industrial or civilian applications has been extremely limited because of its high embodied energy and high cost, despite the fact that employing titanium would significantly reduce energy consumption of mechanical systems such as civilian transportation vehicles, which would have a profound impact on the sustainability of a global economy and the society of the future. Developing a technology to significantly reduce the energy consumption, and thus the cost, of extracting titanium has challenged scientists for nearly a century. In the work described herein, a novel method for extracting titanium metal from upgraded titanium minerals with 60% less energy consumption than conventional methods is discovered. This Communication focuses on the fundamental principles of the new method and the experimental data that demonstrate its feasibility. The methods and data of the energy analysis are documented in the Supporting Information.

The root cause of the high cost of titanium is its very strong affinity for oxygen. A quick reference to the Ellingham diagram of oxides[1] will show that, among common metals, only Al, Mg, Ca, and Li form more stable oxides than Ti. The challenges for producing Ti are not only the extractive processes to separate its oxides from other compounds in Ti feed stocks, but more so the process that reduces titanium oxide to metal. Figure 1

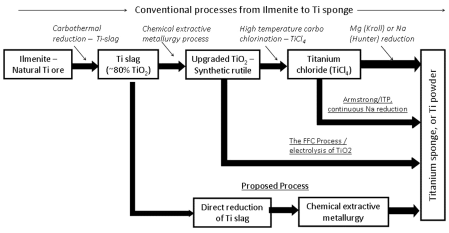

Figure 1. Comparison of conventional and developing processes for production of Ti sponge or Ti powder.

illustrates the major steps of existing methods of producing Ti sponge from ilmenite ore. Over 90% of global titanium reserves is in the form of ilmenite (~45–65% TiO_2 equivalent),[2] with only 10% occurring as natural rutile (~95% TiO_2). Ilmenite can be smelted using a carbothermal process to yield pig iron and Ti-slag.[3] The main component of Ti-slag is ~80% Ti-based oxides which are bonded with other metals in the form of metal titanates,[4] including Fe, Mg, Ca, Al, Si, and other transition metals. Pig iron is used for making iron and steel, whereas the Ti-slag can be used to produce TiO_2 pigment or Ti metal.

The existing technologies, including both commercial and developmental processes, can be categorized into two groups: those by reduction of $TiCl_4$ (e.g., Kroll,[5] Armstrong/ITP[6]) and those by reduction of TiO_2 (e.g., FFC process.[7]) The emphasis in the former approach is to optimize the $TiCl_4$ reduction processes, while the primary motivation of the latter approach is to avoid the high-temperature chlorination process. The Armstrong process is a significant advancement compared to

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Glass formability of W-based alloys through thermodynamic modeling: W–Fe–Hf–Pd–Ta and W–Fe–Si–C

Y.J. Hu [a,*], A.C. Lieser [a], A. Saengdeejing [a], Z.K. Liu [a], L.J. Kecskes [b]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, 304 Steidle Building, University Park, PA 16802, USA
[b] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, RDRL-WMM-F, Aberdeen Proving Ground, MD 21005, USA

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ABSTRACT

Computational thermodynamics, based on the CALculation of PHAse Diagram (CALPHAD) method, can be an efficient way to predict phase stabilities in multi-component engineering materials. By calculating the stability of the liquid phase at low temperatures, this method could be a useful and cost-effective tool for the design of bulk metallic glasses. Based on the thermodynamic modeling of the constituent binary and ternary systems of W with Fe, Hf, Pd, Ta, Si, or C, thermodynamic databases are built to search for W-based metallic glasses in these alloying systems. Modeling of intermetallic phases combines input from first-principles total energy calculations and predictions of finite temperature properties from the Debye–Grüneisen model. Several plausible W-rich glass-forming alloys are identified in the W–Fe–Si–C quaternary system.

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1. Introduction

An inherent drawback of metallic glasses is that they cannot be used at high temperatures because the non-equilibrium glass state may transform to crystalline phases, consequently loosing the excellent properties of metallic glasses. The crystallization temperature of metallic glasses is generally higher for alloys with higher melting points. Because of the advantages of high melting temperature, high density, high modulus of elasticity, and resistance to neutron and gamma radiation, tungsten-based alloys are attractive candidates to identify and synthesize into relevant bulk metallic glasses (BMGs) which, in turn, could be applied as structural materials at high temperatures. In recent experimental efforts, Ohtsuki et al. showed that the formation of W-based BMGs is possible when W is alloyed with precious platinum group metals (PGMs) such as Ru, Ir, and Os [1]. Likewise, Suo et al. reported the possibility of a W–Fe–B–C BMG, though the tungsten content in the composition is low [2]. Hence, it is desirable to develop a systematic methodology to explore the complete compositional space for high W-composition, high density, yet low-cost W-based BMGs.

Glass forming alloys typically consist of multiple elemental species. On one hand, experiments, based on empirically derived algorithms, are prohibitively expensive and time consuming to be an effective search and screening tool in such multi-component BMG systems. On the other hand, it is known that promising glass-forming compositions occur where the liquid is stable at low temperatures, i.e., a deep eutectic [3]. As such, a more viable strategy for predicting glass-forming compositions thus would involve developing and using thermodynamic models of W-based systems to identify deep eutectic liquidus profiles. The CALculation of PHAse Diagram (CALPHAD) method allows one to combine the phase equilibrium and thermodynamic data to evaluate the Gibbs energy descriptions of individual phases in multi-component systems and further build a thermodynamic database [4]. In turn, the liquid phase stability can then be predicted in the entire composition space based on the developed database.

In the present work, Hf and Ta are chosen as possible primary alloying elements as they would maintain the desired high density while Fe, Pd, Si, and C are selected for adding stability to the liquid phase [5]. The databases of two multi-component systems, W–Fe–Hf–Pd–Ta and W–Fe–Si–C, have been established separately by modeling constituent binary and ternary systems based on the CALPHAD method. First-principles calculations are used to predict the enthalpies of formation for intermetallic compounds found in the multi-component systems. Finite temperature thermodynamic data of the intermetallics are obtained using the Debye–Grüneisen model and used in the CALPHAD modeling. Finally, the liquidus projection of each W-contained ternary is calculated and plotted to

* Corresponding author. Tel.: +1 814 863 9957; fax: +1 814 863 4718.
E-mail address: thesunnyhouse@gmail.com (Y.J. Hu).

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Thermal stability and mechanical properties of nanocrystalline Fe–Ni–Zr alloys prepared by mechanical alloying

Hasan Kotan · Kris A. Darling · Mostafa Saber · Ronald O. Scattergood · Carl C. Koch

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Abstract The thermal stability of nanostructured $Fe_{100-x-y}Ni_xZr_y$ alloys with Zr additions up to 4 at.% was investigated. This expands upon our previous results for Fe–Ni base alloys that were limited to 1 at.% Zr addition. Emphasis was placed on understanding the effects of composition and microstructural evolution on grain growth and mechanical properties after annealing at temperatures near and above the bcc-to-fcc transformation. Results reveal that microstructural stability can be lost due to the bcc-to-fcc transformation (occurring at 700 °C) by the sudden appearance of abnormally grown fcc grains. However, it was determined that grain growth can be suppressed kinetically at higher temperatures for high Zr content alloys due to the precipitation of intermetallic compounds. Eventually, at higher temperatures and regardless of composition, the retention of nanocrystallinity was lost, leaving behind fine micron grains filled with nanoscale intermetallic precipitates. Despite the increase in grain size, the in situ formed precipitates were found to induce an Orowan hardening effect rivaling that predicted by Hall–Petch hardening for the smallest grain sizes. The transition from grain size strengthening to precipitation strengthening is reported for these alloys. The large grain size and high precipitation hardening result in a material that exhibits high strength and significant plastic straining capacity.

H. Kotan (✉) · M. Saber · R. O. Scattergood · C. C. Koch
Department of Materials Science and Engineering, NC State University, 911 Partners Way, Room 3078, Raleigh, NC 27695-7907, USA
e-mail: hasankotan@gmail.com

K. A. Darling
Weapons and Materials Research Directorate, RDRL-WMM-F, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069, USA

Introduction

Previous research on mechanically alloyed Fe–Zr alloys [1, 2] showed that additions of 4 at.% Zr can produce stabilization of a nanocrystalline grain size up to temperatures of 900 °C. It was concluded that this would result from a thermodynamic mechanism whereby the oversize Zr atoms segregate to grain boundaries such that the decrease in elastic enthalpy enables a metastable equilibrium at a nanoscale grain size [3–7]. It was also suggested that the bcc-to-fcc phase transition in Fe can lead to a destabilization of the grain size above 900 °C [8]. This effect was confirmed directly in a $Fe_{91}Ni_8Zr_1$ alloy by means of TEM and X-ray diffraction measurements made in situ at temperatures up to 900 °C [9]. Destabilization in this case is observed at 700 °C due to the lower phase transition temperature in Fe–Ni alloys relative to pure Fe. Subsequent to these results, we developed a new regular solution model for thermodynamic stabilization for binary alloys, for example Fe–Zr, which includes both the chemical (bond interaction) and elastic (size misfit) enthalpy effects [6]. A recent extension of this model has been made for ternary alloys, for example, Fe–Ni–Zr [10]. The regular solution model predicts a solubility limit that increases with increasing temperature, the magnitude of which depends on the chemical and elastic enthalpies. Beyond the solubility limit, solute segregates to grain boundaries and the solute excess is only weakly dependent on temperature, with grain boundaries at near full saturation for large misfit oversize solutes like Zr. Therefore, as solute concentration increases above the solubility limit the volume fraction of metastable grain boundaries increases (grain size decreases) in proportion to solute addition and larger solute additions are needed for higher stabilization temperatures. There is also a chemical interaction effect such that thermodynamic stabilization is less effective for Ni additions to Fe (and more effective for

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Structural, elastic, and thermal properties of cementite (Fe_3C) calculated using a modified embedded atom method

Laalitha S. I. Liyanage
Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi 39762, USA and Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, Mississippi 39762, USA

Seong-Gon Kim*
Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi 39762, USA and Center for Computational Sciences, Mississippi State University, Mississippi State, Mississippi 39762, USA

Jeff Houze and Sungho Kim
Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, Mississippi 39762, USA

Mark A. Tschopp
Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, USA

M. I. Baskes
Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California 92093, USA and Los Alamos National Laboratory Los Alamos, New Mexico 87545, USA

M. F. Horstemeyer
Department of Mechanical Engineering, Mississippi State University, Mississippi State, Mississippi 39762, USA and Center for Advanced Vehicular Systems, Mississippi State University, Mississippi State, Mississippi 39762, USA
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Structural, elastic, and thermal properties of cementite (Fe_3C) were studied using a modified embedded atom method (MEAM) potential for iron-carbon (Fe-C) alloys. Previously developed Fe and C single-element potentials were used to develop a Fe-C alloy MEAM potential, using a statistics-based optimization scheme to reproduce structural and elastic properties of cementite, the interstitial energies of C in bcc Fe, and heat of formation of Fe-C alloys in L_{12} and B_1 structures. The stability of cementite was investigated by molecular dynamics simulations at high temperatures. The nine single-crystal elastic constants for cementite were obtained by computing total energies for strained cells. Polycrystalline elastic moduli for cementite were calculated from the single-crystal elastic constants of cementite. The formation energies of (001), (010), and (100) surfaces of cementite were also calculated. The melting temperature and the variation of specific heat and volume with respect to temperature were investigated by performing a two-phase (solid/liquid) molecular dynamics simulation of cementite. The predictions of the potential are in good agreement with first-principles calculations and experiments.

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I. INTRODUCTION

Steel alloys are the most widely used structural materials due to their abundance, all-purpose applicability, and low cost. The main carbide in steel alloys is cementite, which forms a precipitate. Cementite has a direct impact on the mechanical, structural, and thermal properties of steel. Therefore the ability to describe and predict properties of cementite at the nanoscale is essential in the study and design of new steels. Atomistic simulation methods, such as molecular dynamics or Monte Carlo simulations, offer an efficient and reliable route to investigate nanoscale mechanics pertaining to cementite in steel alloys. Each of these methods requires accurate interatomic potentials to find the energy of the system under investigation. However, first-principles calculations, albeit rigorous and accurate, are incapable of simulating the large number of atoms required for realistic calculations due to unreasonable memory and processing-time requirements. Therefore, semiempirical potential methods are being explored as a suitable alternative.

Among the spectrum of semiempirical formulations, the modified embedded atom method (MEAM) [1], originally proposed by Baskes, has been shown to accurately predict properties of most crystal structures, such as bcc, fcc, hcp, and even diatomic gases, in good agreement with experiments or first-principles calculations. MEAM is extended from the embedded atom method (EAM) [2] to include the directionality of bonds. In the original MEAM formalism, only the first-nearest-neighbor (1NN) interactions were considered [1]. Lee *et al.* later extended the original formalism to include the screened second-nearest-neighbor (2NN) interactions [3]. Further details of the MEAM formalism can be found in Refs. [1,3].

One of the commonly used 2NN MEAM potentials for the Fe-C system developed by Lee [4] is designed to predict

*Author to whom correspondence should be addressed: kimsg@ccs.msstate.edu

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An interatomic potential for saturated hydrocarbons based on the modified embedded-atom method

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S. Nouranian,[a] M. A. Tschopp,[ab] S. R. Gwaltney,[c] M. I. Baskes*[d] and M. F. Horstemeyer[ae]

In this work, we developed an interatomic potential for saturated hydrocarbons using the modified embedded-atom method (MEAM), a reactive semi-empirical many-body potential based on density functional theory and pair potentials. We parameterized the potential by fitting to a large experimental and first-principles (FP) database consisting of (1) bond distances, bond angles, and atomization energies at 0 K of a homologous series of alkanes and their select isomers from methane to *n*-octane, (2) the potential energy curves of H_2, CH, and C_2 diatomics, (3) the potential energy curves of hydrogen, methane, ethane, and propane dimers, *i.e.*, $(H_2)_2$, $(CH_4)_2$, $(C_2H_6)_2$, and $(C_3H_8)_2$, respectively, and (4) pressure–volume–temperature (*PVT*) data of a dense high-pressure methane system with the density of 0.5534 g cc^{-1}. We compared the atomization energies and geometries of a range of linear alkanes, cycloalkanes, and free radicals calculated from the MEAM potential to those calculated by other commonly used reactive potentials for hydrocarbons, *i.e.*, second-generation reactive empirical bond order (REBO) and reactive force field (ReaxFF). MEAM reproduced the experimental and/or FP data with accuracy comparable to or better than REBO or ReaxFF. The experimental *PVT* data for a relatively large series of methane, ethane, propane, and butane systems with different densities were predicted reasonably well by the MEAM potential. Although the MEAM formalism has been applied to atomic systems with predominantly metallic bonding in the past, the current work demonstrates the promising extension of the MEAM potential to covalently bonded molecular systems, specifically saturated hydrocarbons and saturated hydrocarbon-based polymers. The MEAM potential has already been parameterized for a large number of metallic unary, binary, ternary, carbide, nitride, and hydride systems, and extending it to saturated hydrocarbons provides a reliable and transferable potential for atomistic/molecular studies of complex material phenomena involving hydrocarbon–metal or polymer–metal interfaces, polymer–metal nanocomposites, fracture and failure in hydrocarbon-based polymers, *etc.* The latter is especially true since MEAM is a reactive potential that allows for dynamic bond formation and bond breaking during simulation. Our results show that MEAM predicts the energetics of two major chemical reactions for saturated hydrocarbons, *i.e.*, breaking a C–C and a C–H bond, reasonably well. However, the current parameterization does not accurately reproduce the energetics and structures of unsaturated hydrocarbons and, therefore, should not be applied to such systems.

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1 Introduction

The embedded-atom method (EAM), developed by Daw and Baskes[1,2] in the early 1980s, is a semi-empirical *N*-body potential useful for the atomistic simulations of metal systems. It has successfully been utilized to calculate the energetics and structures of complex metallic systems involving free surfaces, defects, grain boundaries, *etc.*[3] The potential was later modified by Baskes[4,5] to include the directionality of bonding in covalent materials such as silicon and germanium,[6] leading to the modified embedded-atom method (MEAM)[5] introduced in 1992. It has

[a] *Center for Advanced Vehicular Systems (CAVS), Mississippi State University, Mississippi State, MS 39762, USA*
[b] *Engility Corporation, (on site at) U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA*
[c] *Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, USA*
[d] *Department of Aerospace Engineering, Mississippi State University, Mississippi State, MS 39762, USA. E-mail: baskes@bagley.msstate.edu*
[e] *Department of Mechanical Engineering, Mississippi State University, Mississippi State, MS 39762, USA*

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Atomic-scale analysis of liquid-gallium embrittlement of aluminum grain boundaries

M. Rajagopalan [a], M.A. Bhatia [a], M.A. Tschopp [b], D.J. Srolovitz [c,d], K.N. Solanki [a,*]

[a] School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85281, USA
[b] Dynamic Research Corporation, High Performance Technology Group, (on site at) US Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA
[c] Department of Materials Science & Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
[d] Department of Mechanical Engineering & Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

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Abstract

Material strengthening and embrittlement are controlled by intrinsic interactions between defects, such as grain boundaries (GBs), and impurity atoms that alter the observed deformation and failure mechanisms in metals. In this work, we explore the role of atomistic-scale energetics on liquid-metal embrittlement of aluminum (Al) due to gallium (Ga). Ab initio and molecular mechanics were employed to probe the formation/binding energies of vacancies and segregation energies of Ga for ⟨100⟩, ⟨110⟩ and ⟨111⟩ symmetric tilt grain boundaries (STGBs) in Al. We found that the GB local arrangements and resulting structural units have a significant influence on the magnitude of the vacancy binding energies. For example, the mean vacancy binding energies for ⟨100⟩, ⟨110⟩ and ⟨111⟩ STGBs in the 1st layer was found to be −0.63, −0.26 and −0.60 eV, respectively. However, some GBs exhibited vacancy binding energies closer to bulk values, indicating interfaces with zero sink strength, i.e. these GBs may not provide effective pathways for vacancy diffusion. The results from the present work showed that the GB structure and the associated free volume also play significant roles in Ga segregation and the subsequent embrittlement of Al. The Ga mean segregation energies for ⟨100⟩, ⟨110⟩ and ⟨111⟩ STGBs in the 1st layer were found to be −0.21, −0.09 and −0.21 eV, respectively, suggesting a stronger correlation between the GB structural unit, its free volume and the segregation behavior. Furthermore, as the GB free volume increased, the difference in segregation energies between the 1st layer and the 0th layer increased. Thus, the GB character and free volume provide an important key to understanding the degree of anisotropy in various systems. The overall characteristic Ga absorption length scale was found to be about ∼10, 8 and 12 layers for ⟨100⟩, ⟨110⟩ and ⟨111⟩ STGBs, respectively. In addition, a few GBs of different tilt axes with relatively high segregation energies (between 0 and −0.1 eV) at the boundary were also found. This finding provides a new atomistic perspective for the GB engineering of materials with smart GB networks to mitigate or control liquid-metal embrittlement and more general embrittlement phenomena in alloys.
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Keywords: Liquid metal embrittlement; Atomistic simulation; Grain boundary; Segregation

1. Introduction

Liquid-metal embrittlement (LME) is a phenomenon experienced by many intrinsically ductile metals, including aluminum (Al), nickel (Ni) and copper (Cu). These metals exhibit a drastic loss of ductility in the presence of certain liquid-metals, such as gallium (Ga), bismuth (Bi) and mercury (Hg) [1–10]. Understanding the mechanisms behind LME has been of particular interest in both experimental [2,3,5,8,10–25] and simulation [7,9,26–33] research. Discrepancies between experimental observations and

* Corresponding author. Tel.: +1 (480) 965 1869; fax: +1 (480) 727 9321.
E-mail address: kiran.solanki@asu.edu (K.N. Solanki).

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Grain Boundary Segregation of Interstitial and Substitutional Impurity Atoms in Alpha-Iron

M. RAJAGOPALAN,[1] M. A. TSCHOPP,[2] and K. N. SOLANKI[1,3]

1.—School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287, USA. 2.—U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005, USA. 3.—e-mail: kiran.solanki@asu.edu

The macroscopic behavior of polycrystalline materials is influenced by the local variation of properties caused by the presence of impurities and defects. The effect of these impurities at the atomic scale can either embrittle or strengthen grain boundaries (GBs) within. Thus, it is imperative to understand the energetics associated with segregation to design materials with desirable properties. In this study, molecular statics simulations were employed to analyze the energetics associated with the segregation of various elements (helium, hydrogen, carbon, phosphorous, and vanadium) to four ⟨100⟩ (Σ5 and Σ13 GBs) and six ⟨110⟩ (Σ3, Σ9, and Σ11 GBs) symmetric tilt grain boundaries in α-Fe. This knowledge is important for designing stable interfaces in harsh environments. Simulation results show that the local atomic arrangements within the GB region and the resulting structural units have a significant influence on the magnitude of binding energies of the impurity (interstitial and substitutional) atoms. These data also suggest that the site-to-site variation of energies within a boundary is substantial. Comparing the binding energies of all 10 boundaries shows that the Σ3(112) boundary possesses a much smaller binding energy for all interstitial and substitutional impurity atoms among the boundaries examined in this study. Additionally, based on the Rice–Wang model, our total energy calculations show that V has a significant beneficial effect on the Fe grain boundary cohesion, while P has a detrimental effect on grain boundary cohesion, much weaker than H and He. This is significant for applications where extreme environmental damage generates lattice defects and grain boundaries act as sinks for both interstitial and substitutional impurity atoms. This methodology provides us with a tool to effectively identify the local as well as the global segregation behavior that can influence the GB cohesion.

INTRODUCTION

Increasing global demand for safer, energy-efficient, biocompatible systems for biomedical, transportation, and safety applications requires developing new materials with tuned interface structures.[1] Because the mechanical behavior and fracture of polycrystalline materials is often driven by grain boundaries (GBs) and their underlying structure,[2–4] a fundamental understanding of the relationship between the grain boundary structure and associated properties is important to develop interface-dominant materials. Research has shown that both the macroscopic degrees of freedom and microscopic local structure affect the physical properties of grain boundaries.[5–12] The term *grain boundary character* is often used to describe the 5 degrees of freedom necessary to define a grain boundary. Three degrees of freedom are used to define the misorientation between the two grains and 2 degrees of freedom are associated with the GB plane. In terms of the microscopic local structure, the translations between adjoining grains are also important, as is the localized dislocation structure of the boundary. Historically, many efforts have focused on developing a method to characterize grain boundaries[13–18] and their influence on the physical properties of polycrystalline materials. These

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Grain size stability and hardness in nanocrystalline Cu–Al–Zr and Cu–Al–Y alloys

D. Roy [a,b,*], B.V. Mahesh [c], M.A. Atwater [d], T.E. Chan [a], R.O. Scattergood [a], C.C. Koch [a]

[a] Material Science and Engineering Department, North Carolina State University, Raleigh, NC 27606, USA
[b] Materials and Metallurgical Engineering Department, NIFFT, Ranchi 834003, India
[c] Department of Mechanical and Aerospace Engineering, Monash University, Australia
[d] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, RDRL-WMM-F, Aberdeen Proving Ground, MD 21005-5069, USA

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ABSTRACT

Cryogenic high energy ball milling has been used to synthesize nanocrystalline Cu–14Al, Cu–12Al–2Zr and Cu–12Al–2Y alloys by mechanical alloying. The alloys were studied with the aim of comparing the effect of substituting Y and Zr in place of Al, in Cu–Al alloys, on the grain size stability at elevated temperatures. The as-milled alloys were subjected to annealing at various temperatures between 200 and 900 °C and the resulting grain morphology has been studied using X-ray diffraction and transmission electron microscopy. The addition of Y results in significantly reduced susceptibility to grain growth whereas in case of CuAl and CuAlZr alloys, the susceptibility to grain growth was much higher. The hardness is substantially increased due to Zr and Y addition in the as-milled CuAl powders. However, the hardness of Cu–12Al–2Zr gradually decreases and approaches that of Cu–14Al alloy after the annealing treatment whereas in case of Cu–12Al–2Y alloy, the relative drop in the hardness is much lower after annealing. Accordingly, the efficacy of grain size stabilization by Y addition at high homologous temperatures has been explained on the basis of a recent thermodynamic stabilization models.
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1. Introduction

The study of thermal stabilities of nanocrystalline materials (produced via powder metallurgyroute) against rapid grain growth at elevated temperatures has been of considerable academic interest because the consolidation of nanocrystalline powders to obtain close-to-100% dense bulk materials requires a synergistic effect of high temperature and pressure. A compromise has to be made between good interparticle/intercrystalline bonding and minimal porosityon one hand, and loss of nanocrystallinity via grain coarsening on the other. The time-temperature window for consolidation depends on the susceptibility of the nano-crystalline alloy against significant grain growth. The present study explores the possibility of Zr and Y addition to Cu–14 Al alloy to reduce the susceptibility to grain growth and extend the time-temperature window for the processing of Cu–Al based alloys.

1.1. Grain growth and grain size stabilization in nanomaterials

The primary factor which influences the grain growth in conventional polycrystalline materials is the atomic diffusion in grain boundaries, and the kinetics of grain growth is governed by two significant parameters, namely, activation energy (Q) and the grain boundary exponent (m) [1,2]. A number of investigations have been conducted with the aim of controlling the parameters affecting the grain growth in nanomaterials. The velocity of the grain boundary undergoing a curvature driven growth is given as,

$$v = MP = M_0 \exp\left[\frac{-Q_m}{RT}\right]\frac{2\gamma_b}{r} \quad (1)$$

where M is the mobility, M_o is the pre-exponential constant for mobility term, Q_m is the activation energy for grain boundary mobility, γ_b is the interfacial energy per unit area and r is the radius of the grain. There have been two mechanisms proposed in the literature for reducing the velocity of a moving grain boundary, those being reduction of either the grain boundary mobility 'M' (kinetic stabilization) or the driving force 'P' (thermodynamic stabilization). The thermodynamic stabilization can be accomplished by addition of a solute which lowers the grain boundary energy upon segregation [3–6] as demonstrated in the Fe–Zr system [7]. The kinetic stabilization operates via various mechanisms such as solute drag and pinning of the grain boundaries by pores, inclusions, triple junctions or precipitation at the grain boundaries [1,2,8–10]. The limitation with kinetic stabilization is that the pinning of grain boundaries eventually overcomes by

* Corresponding author. Tel.: +1 919 515 7217; fax: +1 919 515 7724.
E-mail address: droy2k6@gmail.com (D. Roy).

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Generalized stacking fault energy, ideal strength and twinnability of dilute Mg-based alloys: A first-principles study of shear deformation

S.L. Shang [a,*], W.Y. Wang [a], B.C. Zhou [a], Y. Wang [a], K.A. Darling [b], L.J. Kecskes [b], S.N. Mathaudhu [c], Z.K. Liu [a]

[a] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Materials and Manufacturing Sciences Division, US Army Research Laboratory, Aberdeen Proving Ground, MD 21005, USA*
[c] *Materials Science Division, US Army Research Office, Research Triangle Park, NC 27709, USA*

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Abstract

In an effort to establish a scientific foundation for the computational development of advanced Mg-based alloys, a systematic study of the generalized stacking fault (GSF) energy curves has been undertaken. Additionally, the associated stable and unstable stacking and twinning fault energies, ideal shear strengths, and comparative twinnability have been investigated in terms of first-principles calculations for dilute Mg-based alloys of type $Mg_{95}X$. These GSF properties are predicted using the simple and especially the pure alias shear deformations on the basal (0001) plane and along the $[1\,0\,\bar{1}\,0]$ direction of the hexagonal close-packed (hcp) lattice. Fourteen alloying elements (X) are considered herein, namely Al, Ca, Cu, La, Li, Mn, Sc, Si, Sn, Sr, Ti, Y, Zn and Zr. The following conclusions are obtained: (i) the fault energies and the ideal shear strengths of $Mg_{95}X$ alloys decrease approximately linearly with an increasing equilibrium volume of X (or $Mg_{95}X$), with the exceptions being for alloying elements Al, Cu, Si and Zn; (ii) alloying elements Sr and La greatly increase the twin propensity of hcp Mg, while Mn, Ti and Zr exhibit opposite trends; and (iii) the observed variation in GSF properties for hcp Mg caused by alloying elements X can be directly traced to the distribution of the differential charge density ($\Delta\rho$)—a spherical distribution of $\Delta\rho$ facilitates the redistribution of charge and shear deformation, resulting in lower shear-related properties, such as stacking fault energy and ideal shear strength. Computed GSF properties of $Mg_{95}X$ are shown to agree with available experimental and other theoretical results in the literature.
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Keywords: Stacking and twin fault energies; Twin propensity; Ideal shear strength; First-principles calculations; Pure alias shear deformation

1. Introduction

As the lightest metallic structural materials, Mg alloys, which have densities that are approximately two-thirds that of pure aluminum and one-quarter of steel, hold great potential for considerably reducing the weight of vehicles, improving their fuel efficiency, and making them more environmentally friendly [1]. However, Mg-based alloys have poor formability at room temperature due to their limited number of independent slip systems: for instance only two active, independent slip systems on the basal plane exist for Mg and its alloys at room temperature [2]. For the computationally and data-driven development of advanced Mg-based alloys, a complete set of fundamental properties is essential, including assessment of ideal shear strengths and the associated stable and unstable stacking and twin fault energies. Here, the ideal shear strength is a fundamental indicator of material strength [3,4], being related to both the minimum stress needed to plastically deform a perfect single crystal, and the stress required for the formation of stacking faults [4–6]. In addition, the ideal shear strength is also a key parameter to predict the Peierls–Narbarro stress σ_P [7], or the minimum shear stress

* Corresponding author. Tel.: +1 814 8639957; fax: +1 814 8652917.
E-mail address: sus26@psu.edu (S.L. Shang).

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Integrating computational modeling and first-principles calculations to predict stacking fault energy of dilute multicomponent Ni-base alloys

ShunLi Shang [a,*], Yi Wang [a], Yong Du [b], Mark A. Tschopp [c], Zi-Kui Liu [a]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China
[c] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD 21005, USA

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ABSTRACT

Stacking fault energy (γ_{SF}) for dilute multicomponent Ni-base alloys has been modeled using an integrating CALPHAD (calculation of phase diagram) modeling approach and first-principles alias shear deformation calculations of unary, binary, and ternary alloys. The present first-principles results of γ_{SF} from 55 $Ni_{70}X_1Y_1$ (X and Y are 11 alloying elements of Al, Mo, Nb, Os, Re, Ru, Ta, Tc, Ti, V, and W) indicate that the more the structural similarity between X and Y, the smaller the ternary interaction of γ_{SF}; and the variation of γ_{SF} due to alloying elements is similar to that of bulk modulus.

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1. Introduction

A stacking fault (SF) interrupts the stacking sequence of the crystal structure and is important for understanding dislocation behavior in metals [1,2]. For instance, the {1 1 1} stacking sequence of a perfect face-centered cubic (fcc) lattice is ...*ABCABCABC*... with a stacking fault of ...*ABC*|*BCABC*..., where *A*, *B*, and *C* are different {1 1 1} layers and "|" stands for the SF. This can be viewed as a missing *A* layer compared to the perfect fcc lattice or a glide of $a_{fcc}/\sqrt{6}$ (a_{fcc} is the fcc lattice parameter) of the {1 1 1} layer along the $< 1\,1\,\bar{2} >$ direction [3,4]. The associated stacking fault energy (γ_{SF}) is fundamental to our understanding of a vast number of phenomena linked to dislocation, plastic deformation, crystal growth, and phase transition [1–4]. For example, a lower γ_{SF} indicates a larger distance between dislocation partials, a higher twin propensity, and a higher strain-hardening coefficient [1–4], thereby retarding cross-slip and climb even under high stresses and reducing the steady-state creep rate [5–8]. In the present work, γ_{SF} for dilute multicomponent Ni-base alloys with fcc structure will be computed and then modeled as an effort of computational and data-driven materials research.

Although various materials properties of individual phases, including γ_{SF}, can be effectively computed from first-principles calculations, it is not computationally tractable, for the foreseeable future, to use first-principles calculations alone to determine materials properties directly for multicomponent systems, at least not with the accuracy comparable to experimental measurements. In the present work, the general CALPHAD (calculation of phase diagram) approach [9–12] will be used to model the γ_{SF} of Ni-base alloys with input from first-principles calculations. The CALPHAD approach was originally developed for modeling thermodynamic properties by integrating experimental phase equilibrium and thermochemical data [11–13]. The CALPHAD modeling begins by developing models and evaluating parameters of unary and binary systems. By combining the constitutive binary systems with ternary data, ternary interactions and properties of ternary phases are obtained. In this approach, properties of individual phases are modeled and the model parameters are collected in databases, covering the whole composition and temperature ranges, including experimentally uninvestigated regions. Currently, the CALPHAD approach has been extended to model the phase stability, elastic properties [10], molar volumes [14], and diffusion coefficients of multicomponent alloys [15] using input from experiments and first-principles calculations [13]. In the present work, the CALPHAD modeling approach will be employed to model the stacking fault energy of the dilute multicomponent Ni-base alloys.

The CALPHAD modeling of properties in multicomponent systems can be written in a general form as follows [9,10],

$$\phi = {}^{0}\phi + \Delta\phi \quad (1)$$

* Corresponding author. Tel.: +1 8148639957; fax: +1 8148652917.
E-mail address: sus26@psu.edu (S. Shang).

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A rate dependent constitutive model for ECAE Cu based on instrumented nanoindentation results

J. Su [a,b], W.G. Guo [b], L.J. Kecskes [c], S.N. Mathaudhu [c], Q. Wei [a,*]

[a] Department of Mechanical Engineering, University of North Carolina at Charlotte, Charlotte, NC 28223-0001, USA
[b] School of Aeronautics, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China
[c] WMRD, US Army Research Laboratory, Aberdeen Proving Ground, MD 21005-5069, USA

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ABSTRACT

We have investigated the plastic deformation behavior, especially the strain rate sensitivity of Cu, subjected to severe plastic deformation via equal channel angular extrusion (ECAE) with a varying number of passes. We have performed nanoindentation strain rate jump experiments to measure the hardness values at different loading rates, and determine the strain rate sensitivity (SRS). In turn, the activation volume (V^*) associated with plastic deformation of the ECAE Cu has been derived and analyzed. Based on the dislocation-mediated processes during ECAE, including dislocation accumulation, dynamic recovery and recrystallization, combined with creep theory, a strain rate dependent constitutive model has been constructed for the ECAE Cu. We have reached good agreement between the model predictions and the experimental results. It was found that the model can provide a plausible understanding of the various aspects of the mechanical behavior of the ECAE Cu.

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1. Introduction

Severe plastic deformation (SPD) is one of several efficient processes to refine grain size and to obtain ultrafine-grained (UFG, grain size, d, smaller than 1000 nm, but greater than 100 nm) and nanocrystalline (NC, $d < 100$ nm) materials. Different forms of SPD such as equal channel angular pressing or extrusion (ECAP or ECAE) [1], accumulative roll-bonding (ARB) [2], high-pressure torsion (HPT) [3] etc. have been widely utilized both in industry and research laboratories. Estrin et al. [4] gave a brief review of the various SPD techniques in the diamond jubilee issue of Acta Materialia to recount the historic milestones in this area. As one of the most popular SPD techniques, ECAE has been demonstrated to be highly efficient in improving the strength with a relatively small loss of ductility by refining the grain size. Numerous articles have been published since Segal [5] invented the technique in 1977 and was granted a US patent in 1996. The basic operating conditions such as those of pure and simple shear, the total strain, equivalent strain during each pass using different route orientations, and deformation mode and history have been extensively enumerated [6–11]. Since then, many research groups have made further contributions to the development of the ECAE technique. Azushima [12], Valiev [13], and Zhu [14], for example, have developed the basic theoretical understanding, articulated the currently accepted technical extrusion routes and, more broadly, various applications of the different SPD processes to produce UFG metals and alloys. The key properties of SPD processed nanostructured materials have been evaluated and tabulated, including their fundamental physical parameters (diffusivity, elasticity, and internal friction), mechanical properties (strengthening behavior, ductility, fatigue, and super-plasticity), and other physical and engineering properties (magnetic hysteresis, optical properties of semiconductors, and corrosion behavior) and the potential practical applications have been discussed. Many authors [2,15–27] have published on the SPD processing of metals, particularly, using the ECAE technique. These investigations include copper, nickel, aluminum, titanium, tantalum, iron, tungsten, niobium, as well as many alloys. Specifically, processing induced microstructural evolution and structure-property relationships have been examined.

However, there are still many unresolved and outstanding issues that remain, particularly associated with the deformation mechanisms of UFG/NC metals produced by various SPD techniques. As such, efforts to achieve better and deeper understanding of the mechanical behavior of these SPD processed UFG metals and alloys have been continued. Significant progress has been made with the help of advanced techniques such as transmission electron microscopy (TEM), electron backscatter diffraction (EBSD), or orientation imaging microscopy (OIM). For example, EBSD analysis has shown that the fraction of high angle grain boundaries (HAGBs) of ECAE Nb and Cu continue to increase with

* Corresponding author. Tel.: +1 704 687 8213; fax: +1 704 684 8345.
E-mail address: qwei@uncc.edu (Q. Wei).

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Binding energetics of substitutional and interstitial helium and di-helium defects with grain boundary structure in α-Fe

M. A. Tschopp,[1,2,a)] F. Gao,[3] L. Yang,[3] and K. N. Solanki[4]
[1]*Dynamic Research Corporation, (on site at) U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, USA*
[2]*Center for Advanced Vehicular Systems, Mississippi State University, Starkville, Mississippi 39762, USA*
[3]*Pacific Northwest National Laboratory, Richland, Washington 99352, USA*
[4]*Arizona State University, School for Engineering of Matter, Transport and Energy, Tempe, Arizona 85287, USA*

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The formation/binding energetics and length scales associated with the interaction between He atoms and grain boundaries in BCC α-Fe were explored. Ten different low Σ grain boundaries from the ⟨100⟩ and ⟨110⟩ symmetric tilt grain boundary systems were used. In this work, we then calculated formation/binding energies for 1–2 He atoms in the substitutional and interstitial sites (HeV, He_2V, HeInt, He_2Int) at all potential grain boundary sites within 15 Å of the boundary (52 826 simulations total). The present results provide detailed information about the interaction energies and length scales of 1–2 He atoms with grain boundaries for the structures examined. A number of interesting new findings emerge from the present study. For instance, the Σ3(112) twin boundary in BCC Fe possesses a much smaller binding energy than other boundaries, which corresponds in long time dynamics simulations to the ability of an interstitial He defect to break away from the boundary in simulations on the order of nanoseconds. Additionally, positive correlations between the calculated formation/binding energies of the He defects ($R > 0.9$) asserts that the local environment surrounding each site strongly influences the He defect energies and that highly accurate quantum mechanics calculations of lower order defects may be an adequate predictor of higher order defects. Various metrics to quantify or classify the local environment were compared with the He defect binding energies. The present work shows that the binding and formation energies for He defects are important for understanding the physics of He diffusion and trapping by grain boundaries, which can be important for modeling He interactions in polycrystalline steels. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861719]

I. INTRODUCTION

Understanding radiation damage phenomena in nuclear materials is important for predicting the mechanical behavior of current and future nuclear power reactors.[1] In particular, future fusion reactors will produce a much larger amount of both He and H as compared to fission reactors, hence the microstructure of the structural materials used in fusion reactors will be much more sensitive to interactions with He defects.[2,3] In terms of radiation damage, the production of helium through (n,α) transmutation reactions causes both microstructure evolution and drastic property changes in the first-wall and blanket structural materials of fusion reactors. The production of single helium atoms and small He clusters in the metal lattice is inherently a problem that occurs at the nanoscale. The subsequent diffusion of He and He clusters results in the nucleation and growth of He bubbles on grain boundaries and within the lattice, which lead to a macroscopic deterioration of material properties including void swelling, surface roughening and blistering, and high temperature intergranular embrittlement.[1–9] While the production and diffusion of He occurs at the nanoscale, these other processes develop at larger length scales over long time scales, which necessitates developing predictive multiscale models for material behavior under irradiation conditions that couples multiple simulation methods at different length and time scales. Developing this predictive capability will require an understanding of the mechanisms associated with radiation damage phenomena, of the He interaction with microstructures, and of the associated uncertainties.

It is well known that He interactions in Fe play an important role in the mechanical behavior of steel alloys. There have been a number of quantum mechanics and molecular dynamics simulations that have examined how He and He clusters affect single crystal lattice properties and physical properties in α-Fe.[10–29] For instance, density functional theory (DFT) simulations have been used to show that interstitial He atoms strongly interact with vacancies and can also be trapped by interstitial atoms (binding energy of 0.3 eV).[10] Ventelon, Wirth, and Domain[24] probed the interactions between He and self-interstitial atoms (SIAs) in α-Fe and found strong binding behavior between interstitial He and SIA clusters, which corresponded with the SIA defect strain field. Other atomistic studies have examined how He and H interact within the single crystal lattice to form complex He–H clusters[27,28] or how He impacts the production of irradiation-induced point defects in an Fe–Cr matrix.[29] Stewart *et al.*[25,26] recently used several Fe-He potentials[30–32] to show the effect of the interatomic potential on the

[a)]Author to whom correspondence should be addressed. Electronic mail: mark.tschopp@gatech.edu

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Binding of He_nV clusters to α-Fe grain boundaries

M. A. Tschopp,[1,a)] F. Gao,[2] and K. N. Solanki[3]
[1]*U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, USA*
[2]*Pacific Northwest National Laboratory, Richland, Washington 99352, USA*
[3]*Arizona State University, Tempe, Arizona 85287, USA*

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The objective of this research is to explore the formation/binding energetics and length scales associated with the interaction between He_nV clusters and grain boundaries in bcc α-Fe. In this work, we calculated formation/binding energies for 1–8 He atoms in a monovacancy at all potential grain boundary (GB) sites within 15 Å of the ten grain boundaries selected (122106 simulations total). The present results provide detailed information about the interaction energies and length scales of 1–8 He atoms with grain boundaries for the structures examined. A number of interesting new findings emerge from the present study. First, the Σ3(112) "twin" GB has significantly lower binding energies for all He_nV clusters than all other boundaries in this study. For all grain boundary sites, the effect of the local environment surrounding each site on the He_nV formation and binding energies decreases with an increasing number of He atoms in the He_nV cluster. Based on the calculated dataset, we formulated a model to capture the evolution of the formation and binding energy of He_nV clusters as a function of distance from the GB center, utilizing only constants related to the maximum binding energy and the length scale. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4883357]

I. INTRODUCTION

The ability to predict the mechanical behavior of current and future nuclear power reactors necessitates understanding the atomic interactions associated both with radiation damage phenomena and grain boundaries in polycrystalline nuclear materials.[1] In particular, future fusion reactors will produce a much larger amount of both He and H as compared to fission reactors, hence the microstructure of the structural materials used in fusion reactors will be much more sensitive to interactions with He defects.[2,3] In terms of radiation damage, the production of helium through (n, α) transmutation reactions causes both microstructure evolution and drastic property changes in the first-wall and blanket structural materials of fusion reactors. The production of single helium atoms and small He clusters in the metal lattice is inherently a problem that occurs at the nanoscale. The subsequent diffusion of He and He clusters results in the nucleation and growth of He bubbles on grain boundaries and within the lattice, which lead to a macroscopic deterioration of material properties including void swelling, surface roughening and blistering, and high temperature intergranular embrittlement [e.g., Refs. 1–9]. While the production and diffusion of He occurs at the nanoscale, these other processes develop at larger length scales over long time scales, which necessitates developing predictive multiscale models for material behavior under irradiation conditions that couples multiple simulation methods at different length and time scales. Developing this predictive capability will require an understanding of the mechanisms associated with radiation damage phenomena, of the He interaction with microstructures and of the associated uncertainties.

It is well known that He interactions in Fe play an important role in the mechanical behavior of steel alloys. There have been a number of quantum mechanics and molecular dynamics simulations that have examined how He and He clusters affect single crystal lattice properties and physical properties in α-Fe.[10–28] For instance, density functional theory (DFT) simulations have been used to show that interstitial He atoms strongly interact with vacancies and can also be trapped by interstitial atoms (binding energy of 0.3 eV).[10] Ventelon, Wirth, and Domain[24] probed the interactions between He and self-interstitial atoms (SIAs) in α-Fe and found strong binding behavior between interstitial He and SIA clusters, which corresponded with the SIA defect strain field. Other atomistic studies have examined how He and H interact within the single crystal lattice to form complex He–H clusters[27] or how He impacts the production of irradiation-induced point defects in an Fe–Cr matrix.[28] Stewart *et al.*[25,26] recently used several Fe–He potentials[29–31] to show the effect of the interatomic potential on the resulting dynamics of He transport and He clustering in Fe. Ascertaining the reactions that occur and quantifying their energetics are important for a fundamental understanding of how point defects, impurities, substitutional atoms, and helium atoms interact in the single crystal lattice of α-Fe. Furthermore, this information is useful for models that explore the kinetics of He diffusion, trapping (clustering), and detrapping (emission), such as rate theory models,[32–35] kinetic Monte Carlo models,[36,37] and/or phase field models.[38,39]

The grain boundary itself and its atomic configuration within these alloy systems plays a significant role in trapping

[a)]Author to whom correspondence should be addressed. Electronic mail: mark.a.tschopp.civ@mail.mil

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"Bulk" Nanocrystalline Metals: Review of the Current State of the Art and Future Opportunities for Copper and Copper Alloys

M.A. TSCHOPP,[1,2] H.A. MURDOCH,[1] L.J. KECSKES,[1] and K.A. DARLING[1]

1.—U.S. Army Research Laboratory, Aberdeen Proving Ground, Aberdeen, MD 21005, USA.
2.—e-mail: mark.tschopp@gatech.edu

It is a new beginning for innovative fundamental and applied science in nanocrystalline materials. Many of the processing and consolidation challenges that have haunted nanocrystalline materials are now more fully understood, opening the doors for bulk nanocrystalline materials and parts to be produced. While challenges remain, recent advances in experimental, computational, and theoretical capability have allowed for bulk specimens that have heretofore been pursued only on a limited basis. This article discusses the methodology for synthesis and consolidation of bulk nanocrystalline materials using mechanical alloying, the alloy development and synthesis process for stabilizing these materials at elevated temperatures, and the physical and mechanical properties of nanocrystalline materials with a focus throughout on nanocrystalline copper and a nanocrystalline Cu-Ta system, consolidated via equal channel angular extrusion, with properties rivaling that of nanocrystalline pure Ta. Moreover, modeling and simulation approaches as well as experimental results for grain growth, grain boundary processes, and deformation mechanisms in nanocrystalline copper are briefly reviewed and discussed. Integrating experiments and computational materials science for synthesizing bulk nanocrystalline materials can bring about the next generation of ultrahigh strength materials for defense and energy applications.

INTRODUCTION

Mechanical Properties of Nanocrystalline Materials

Nanocrystalline materials result from the grain size of polycrystalline materials being reduced through processing to dimensions on the order of nanometers, which corresponds to drastic increases in the volume fraction (and importance) of grain boundaries and triple junctions within the material. For instance, Fig. 1 shows the evolution of the volume fraction of grain boundaries and triple junctions as a function of grain size, assuming an idealized tetrakaidecahedra grain structure with a grain boundary thickness of 1 nm (solid line). Notice that for grain sizes on the order of 30 nm and smaller, the volume fraction of grain boundaries reaches 10%—approximately an order of magnitude greater than ultrafine grained materials (100 nm to 1000 nm) and several orders of magnitude greater than most coarse-grained polycrystalline materials—which profoundly affects their physical and mechanical behavior.

The interest in nanocrystalline (nc) and ultrafine-grained materials has been motivated by potential improvements in mechanical properties over coarser grained polycrystalline materials[1–5] through the classic Hall–Petch relationship,[6,7] which is defined as

$$\sigma_Y = \sigma_0 + \frac{k}{\sqrt{d}} \quad (1)$$

In this equation, σ_Y is the yield stress, σ_0 is the friction stress required to move individual dislocations, k is a constant, and d is the grain size. The increase in yield strength with decreasing

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Characterizing the Local Primary Dendrite Arm Spacing in Directionally Solidified Dendritic Microstructures

MARK A. TSCHOPP, JON D. MILLER, ANDREW L. OPPEDAL, and KIRAN N. SOLANKI

Characterizing the spacing of primary dendrite arms in directionally solidified microstructures is an important step for developing process–structure–property relationships by enabling the quantification of (i) the influence of processing on microstructure and (ii) the influence of microstructure on properties. In this work, we utilized a new Voronoi-based approach for spatial point pattern analysis that was applied to an experimental dendritic microstructure. This technique utilizes a Voronoi tessellation of space surrounding the dendrite cores to determine nearest neighbors and the local primary dendrite arm spacing. In addition, we compared this technique to a recent distance-based technique and a modification to this using Voronoi tessellations. Moreover, a convex hull-based technique was used to include edge effects for such techniques, which can be important for thin specimens. These methods were used to quantify the distribution of local primary dendrite arm spacings, their spatial distribution, and their correlation with interdendritic eutectic particles for an experimental directionally solidified Ni-based superalloy micrograph. This can be an important step for correlating processing and properties in directionally solidified dendritic microstructures.

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I. INTRODUCTION

DEVELOPING an enhanced understanding of mechanical behavior in materials relies upon sufficiently characterizing microstructure details at the relevant length scales that contribute to this behavior. Moreover, to truly enhance the predictive capability of processing–structure–property models that aim to improve material performance requires a quantitative stereological description of the relevant microstructure features and, thereby, the material itself. Predictive models that effectively capture the linkage between processing and properties (through microstructure) can be utilized within an integrated computational materials engineering (ICME) approach to design materials and accelerate their insertion into application.

The focus of the present work is on single-crystal nickel-based superalloys, which are used in turbine blades within the high temperature section of the modern turbine engine.[1,2] In single-crystal nickel-based superalloys, there are a number of length scales of microstructure that contribute to mechanical behavior, ranging from the γ' precipitates to pores and eutectic particles to the dendrites themselves. At the largest microstructure length scale in directionally solidified single-crystal microstructures, the features of interest are the dendrites; many features at lower length scales (*e.g.*, eutectic particles, precipitates, *etc.*) or at similar scales (*e.g.*, porosity, freckle defects, *etc.*) are strongly associated with the dendrite arm spacing and morphology.[3–7] The solidification morphology associated with dendrite arm spacing has been described in the literature.[8,9] Historically, the primary dendrite arm spacing (PDAS) has been found to correlate with processing (*e.g.*, solidification rate)[7,10–14] as well as with properties (*e.g.*, creep strength, fatigue properties).[15,6] For instance, Lamm and Singer[6] produced single-crystal nickel-based microstructures (PWA 1483) with a varied range of different dendrite arm spacings (250 to 600 μm) and found that decreasing the mean dendrite arm spacing was associated with an increased high-cycle fatigue life. The fatigue cracks were found to originate at shrinkage porosity and the largest pores correlated with a large PDAS.

The traditional approach for measuring PDAS in single-crystal metals, whereby the number of dendrite cores in a specified area is related to the dendrite arm spacing[10,16,17] is given by:

$$\lambda = c\sqrt{\frac{A}{n}}, \qquad [1]$$

where λ is PDAS, A is the area analyzed, n is the number of dendrites, and c is a coefficient that depends on the microstructure. McCartney and Hunt[10] showed that $c = 0.5$ for a random array of points, $c = 1$ for a

MARK A. TSCHOPP, Senior Research Scientist, is with the Lightweight and Specialty Metals Branch, Materials and Manufacturing Science Division, Army Research Laboratory, Aberdeen Proving Ground, MD 21005, and also with the Center for Advanced Vehicular Systems, Mississippi State University, Starkville, MS 39759. Contact e-mail: mark.a.tschopp.ctr@mail.mil JON D. MILLER, Senior Materials Research Engineer, is with the Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH 45433. ANDREW L. OPPEDAL, Postdoctoral Associate, is with the Center for Advanced Vehicular Systems, Mississippi State University. KIRAN N. SOLANKI, Assistant Professor, is with the School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287.
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MATERIALS RESEARCH LETTERS

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Effects of Alloying Elements on Stacking Fault Energies and Electronic Structures of Binary Mg Alloys: A First-Principles Study

William Yi Wang[a,d*], Shun Li Shang[a], Yi Wang[a], Zhi-Gang Mei[a], Kristopher A. Darling[c], Laszlo J. Kecskes[c], Suveen N. Mathaudhu[b], Xi Dong Hui[d] and Zi-Kui Liu[a]

[a]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA; [b]Materials Science Division, U.S. Army Research Office, Research Triangle Park, NC 27709, USA; [c]U.S. Army Research Laboratory, Weapons and Materials Research Directorate, RDRL-WMM-B, Aberdeen Proving Ground, MD 21005, USA; [d]State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

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The growth, deformation, and extrinsic faults in binary Mg–X alloys are investigated via first-principles calculations. Here, the alloying elements X include Al, Ca, Cu, Fe, K, La, Li, Mn, Na, Nd, Pr, Si, Sn, Sr, Y, Zn, and Zr. In addition to stacking fault energies, the effect of the elements on the bond structure of Mg are studied in term of electron localization morphology. It is observed that rod-like directional bonds in non-fault planes transform into tetrahedral morphologies in fault planes and are strengthened by addition of Zn and Al, but weakened by Na.

Keywords: Magnesium Alloys, Alloying Elements, Stacking Faults, First-Principles Calculations

With a density that is two-thirds of aluminum or one-quarter of steel, Mg alloys are important structural materials for vehicles to improve fuel economy and reduce emissions.[1] The stacking fault energy, γ_{sf}, is an important property dictating deformation in Mg alloys.[2] It is closely related to the core structure and the mobility of the dislocations.[3–7] The reduction of γ_{sf} could enhance the twinnability of the material,[8,9] increase the ductility,[10–12] and reduce the steady-state creep rate.[13,14] The stacking sequence of an ideal HCP metal metal is . . .ABABABAB. . . with A, B, (or C, see below) being different {0001} planes. There are three types of stacking faults commonly studied, i.e. growth fault (I1), deformation fault (I2), and extrinsic fault (EF). An I1 fault is formed by removing an A plane above a B plane, and then shearing the remaining planes above the B plane by $\frac{1}{3}[1\bar{1}00]$, resulting in . . .ABA$\dot{\text{B}}$CBCB. . . with the fault layer marked with a dot on top of it (same below). An I2 fault is formed by a shearing of $\frac{1}{3}[1\bar{1}00]$, resulting in . . .ABA$\dot{\text{B}}\dot{\text{C}}$ACA. . . . [4,15] An EF fault is generated by inserting an extra C plane into the ideal HCP structure, resulting in . . .ABA$\dot{\text{B}}\dot{\text{C}}\dot{\text{A}}$BAB. . . .

Recently, electronic structures have been used to gain insights into mechanical properties of materials.[16–19] For example, first-principles calculations based on density functional theory [20] indicate correlations between the elastic properties of Al, its bonding electrons, and the electrostatic potential distributions through the deformation electron density,[16] $\Delta\rho$, defined as the difference between the total electron density (ρ_{total}) and the electron density associated with unbounded atoms (ρ_{IAM}). In a previous work,[21] we found that the number of atomic layers affected by the presence of the stacking fault increases in the order of I1, I2, and EF in accordance with their stacking fault energies. Additionally, quantitative evaluations of charge density reveal that the redistribution range of deformation electron density along the [0001] direction is closely related to stacking fault energy.

Theoretical investigations of stacking fault energies of some binary Mg–X alloys have recently been reported in the literature [22–25] along with contour plots of electron density in 2D and electron density isosurface figures in 3D,[26–30] however, the detailed chemical bond structures of the fault and non-fault layers and the

*Corresponding author. Emails: yuw129@psu.edu, billyi.wang@gmail.com

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Wang WY, Shang SL, Wang Y, Mei ZG, Darling KA, Kecskes LJ, Mathaudhu SN, Hui XD, Liu ZK. Effects of alloying elements on stacking faults energies and electronic structures of binary Mg alloys: A first-principles study. Materials Research Letters. 2014;2(1):29–36. Open Access article distributed under the terms of the Creative Commons Attribution License.

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Electronic structures of long periodic stacking order structures in Mg: A first-principles study

William Yi Wang [a,b,*], Shun Li Shang [a], Yi Wang [a], Kristopher A. Darling [b], Laszlo J. Kecskes [c], Suveen N. Mathaudhu [d], Xi Dong Hui [b], Zi-Kui Liu [a,*]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China
[c] U.S. Army Research Laboratory, Weapons and Materials Research Directorate, RDRL-WMM-B, Aberdeen Proving Ground, MD 21005, USA
[d] Materials Science Division, U.S. Army Research Office, Research Triangle Park, NC 27709, USA

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ABSTRACT

Long period stacking order (LPSO) structures, such as 6H, 10H, 14H, 18R and 24R, play significant roles in enhancing the mechanical properties of Mg alloys and have been largely investigated separately. In the present work, through detailed investigations of deformation electron density, we show that the electron structures of 10H, 14H, 18R and 24R LPSO structures in Mg originate from those of deformation stacking faults in Mg, and their formation energies can be scaled with respect to formation energy and the number of layers of deformation stacking faults, while the electron structure and formation energy of the 6H LPSO structure are between those of deformation and growth stacking faults. The simulated images of high resolution transmission electron microscopy compare well with experimental observed ones. The understanding of LPSO structures in Mg enables future quantitative investigations of effects of alloying elements on properties of LPSO structures and Mg alloys.

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1. Introduction

As the lightest metallic structural materials, Mg alloys are particularly attractive for transportation applications such as automobiles and aircrafts for weight reducing and higher fuel efficiency [1]. Numerous efforts have been made in order to increase the strength and the ductility of Mg alloys. In recent years, Mg-RE alloys with excellent mechanical properties have been obtained for combining fine grain size, precipitates, and long period stacking order (LPSO) structures. For instance, the tensile yield strength and the elongation of $Mg_{97}Y_2Zn_1$ (at.%) alloy with the 6H LPSO structure produced by rapid solidification can reach 610 MPa and 5%, respectively, with grain sizes in range of 100 nm–150 nm [2]. When the grain size of Mg matrix is about 330 nm, the tensile yield strength and the elongation become 400 MPa and 2%, respectively [3]. It is commonly accepted that fine precipitates or local clustering of solute atoms together with different types of LPSO structures, including 6H, 10H, 14H, 18R and 24R, contribute to strengthening of Mg alloys [4–13].

The 6H, 10H, 14H, 18R and 24R LPSO structures have been reported in Mg alloys by atomic-resolution Z-contrast scanning transmission electron microscopy (STEM) [2,4,12,14–16] and are typically characterized by their stacking sequence of close packed planes as listed in Table 1. It has been estimated that the formation energy of 6H twice that of the growth fault (I1), while the formation energies of other LPSO structures depend on the number of the deformation fault (I2) they contain [17]. The ABCA-type stacking sequence in I2, 14H and 18R are similar, but with distinct spatial arrangements [16,18]. This similarity has in some cases led to transformations between variant structure, such as 18R to 14H observed at high temperature by transmission electron microscopy (TEM) in a Mg–2Zn–8Y–0.6Zr (wt%) alloy [16]. Such intricate connections among stacking faults and all LPSO structure have not been fully explored and understood, particularly the electronic structures of various LPSO structures and their dependences on alloying elements. Experimentally, the technique of electron tomography provides not only the atomic structure, but also the electronic structures together with simulations based on density functional theory (DFT) [19], such as the nature of chemical bond and the charge redistribution [20–25]. It is noted that the electron density predicted from DFT-based first-principles calculations can be directly compared with the charge transfer obtained from electron tomography measurements and used to simulate the HRTEM images by projecting the electron density or converting the electron density into electron scattering factor [25–28].

* Corresponding authors. Address: Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 814 8651934, fax: +1 707 8851934 (Z.-K. Liu), tel.: +1 814 863 9957 (W.Y. Wang).
E-mail addresses: yuw129@psu.edu (W.Y. Wang), dr.liu@psu.edu (Z.-K. Liu).

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Algorithm Development in Computational Materials Science

JONATHAN A. ZIMMERMAN,[1,6] ADRIAN S. SABAU,[2] MOHSEN ASLE ZAEEM,[3] MARK A. TSCHOPP,[4] and DOUGLAS E. SPEAROT[5]

1.—Mechanics of Materials Department, Sandia National Laboratories, Livermore, CA 94550, USA. 2.—Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. 3.—Materials Science & Engineering Department, Missouri University of Science and Technology, Rolla, MO 65409, USA. 4.—Materials and Manufacturing Science Division, U.S. Army Research Laboratory, Adelphi, MD 20783, USA. 5.—Department of Mechanical Engineering, University of Arkansas, Fayetteville, AR 72701, USA. 6.—e-mail: jzimmer@sandia.gov

Computational modeling and simulation are among the areas of research, development, and application that have had the most impact on the field of materials science and engineering. This fact was recently underscored when the 2013 Nobel Prize in Chemistry was awarded to Martin Karplus, Michael Levitt, and Arieh Warshel for developing multiscale models for complex chemical systems. This accomplishment—made initially in the mid-1970s—affirms the role that numerical simulation has on elucidating the physical behavior of materials and development of new materials. It also highlights that in an arena where computers are tasked with doing the 'heavy lifting' of mathematical calculations, innovation is still needed to leverage their power to attain true scientific achievement. For instance, the work by Karplus, Levitt, and Warshel is notable not only for developing and implementing a computer program to compute π-electron and vibration spectra of planar molecules but also for coupling classic and quantum approaches to enable a computationally efficient approach that made modeling the phenomenon of protein folding a feasible endeavor.

Today, the use of computation in materials research is far more pervasive than it was in the 1970s, and while the resources available in the 21st century far surpass those available to Karplus, Levitt, and Warshel in the 1970s, the need for innovative techniques and algorithms is no less critical. Just as computational power has grown dramatically since those early days, so too have increased the number and complexity of methods by which modeling, simulation, and analysis is done. These methods exist over a gamut of length and time scales, and they include techniques such as density functional theory, interatomic potential (i.e., force field)-based molecular dynamics, the Monte Carlo method, discrete dislocation dynamics, cellular automata method, the phase-field method, finite-element analysis, and many more. While the foundations of all of these approaches already exist, the development of solution algorithms is ongoing to enable the treatment of increasingly complex systems and materials over longer spans of simulated time in an acceptable amount of computational time. The complexity of multiscale and multiphysics models is the key issue, with the goal of improving the representation of the relevant physical and chemical processes being paramount. Strategies to achieve this complexity vary from extending existing methods into foreign regimes of length–time–energy–phase space, to the coupling of multiple methods, each firmly rooted in its own regime, to the design of new methods that explore this landscape in unique and novel ways.

Developing, implementing, and executing simulation methods is only half of the challenges faced by the modern computational scientist. Data analysis and characterization of computer simulation results that are relevant to each computational approach require an equal effort developing techniques and tools able to sift through gigabytes to terabytes of data and delivering insights on the simulated structures and processes. For example, to study defects in crystalline media during atomistic simulation, common neighbor analysis,[1] centrosymmetry parameter,[2] and the dislocation extraction algorithm[3] represent a few notable developments that have enabled characterizing material structure within simulated configurations. These insights necessitate not only the efficient calculation of experimentally measurable characteristics of material systems but also the theoretical development of new metrics that offer new understanding not provided by experiments.

The need for innovation in algorithm development is not restricted to activities of the computational theoretician. The hardware and techniques available to the experimental materials scientist have also evolved over time, necessitating algorithms that expand the frontiers of data acquisition and analysis. Approaches for extracting useful information from large sets of data—known as data

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Appendix B. FY14 ARL Technical Publications

This appendix appears in its original form, without editorial change.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005

ARL-TR-6743 **December 2013**

Enhancing the High Temperature Capability of Nanocrystalline Alloys: Utilizing Thermodynamic Stability Maps to Mitigate Grain Growth Through Solute Selection

Mark A. Tschopp and Kristopher A. Darling
Weapons and Materials Research Directorate

Mark A. Atwater
Applied Engineering, Safety & Technology Department
Millersville University

Brian K. VanLeeuwen and Zi-Kui Liu
Department of Materials Science and Engineering
Pennsylvania State University

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-6788 **January 2014**

Ultrahigh-Strength Magnesium Alloys for the Future Force: A Final Report on the 5-Year Mission Program, 2009–2013

Vincent Hammond, Suveen Mathaudhu, Kevin Doherty, Shawn Walsh, Lionel Vargas, Brian Placzankis, Joseph Labukas, Marc Pepi, Matt Trexler, Blake Barnett, Tyrone Jones, and Laszlo Kecskes

Weapons and Materials Research Directorate, ARL

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Army Research Laboratory
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ARL-TR-6807 **February 2014**

Evaluation of an Al, La Modified $MgZn_2Y_2$ Alloy

Vincent H. Hammond, Tomoko Sano, Joseph P. Labukas, Teresa A. Dillon, and Brady G. Butler
Weapons and Materials Research Directorate, ARL

Jianghua Shen and Qiuming Wei
University of North Carolina - Charlotte

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Army Research Laboratory
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ARL-TR-6885 **April 2014**

Effect of Cleanliness on Hydrogen Tolerance in High-Strength Steel

Scott M. Grendahl
Weapons and Materials Research Directorate, ARL

Franklyn Kellogg and Hoang Nguyen
Bowhead Technical Services

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-7027 **August 2014**

Reactivity of Aluminum-Based Mixtures with Early Transition Metals

Laszlo J Kecskes and Kenneth F Plunkett
Weapons and Materials Research Directorate, ARL

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-MR-856 **November 2013**

The Influence of Novel Alloying Additions on the Performance of Magnesium Alloy AZ31B

Kateryna Gusieva and Nick Birbilis
Department of Materials Engineering, Monash University (Australia)

Vincent H. Hammond, Joseph P. Labukas, and Brian E. Placzankis
Weapons and Materials Research Directorate, ARL

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Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-RP-485 **June 2014**

‘‘Bulk’’ Nanocrystalline Metals: Review of the Current State of the Art and Future Opportunities for Copper and Copper Alloys

M. A. Tschopp, H. A. Murdoch, L. J. Kecskes, and K. A. Darling
Weapons and Materials Research Directorate, ARL

A reprint from *JOM*, Vol. 66, No. 6, pp. 1000–1019, 2014.

Approved for public release; distribution is unlimited.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-RP-0491 **July 2014**

Cobalt-Base Alloy Gun Barrel Study

William S. de Rosset and Jonathan S. Montgomery
Weapons and Materials Research Directorate, ARL

A reprint from the *Wear*, Vol. 316, pp. 119–123, 14 May 2014.

Approved for public release; distribution is unlimited.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-RP-0496 **July 2014**

Microstructure and Mechanical Properties of Bulk Nanostructured Cu–Ta Alloys Consolidated by Equal Channel Angular Extrusion

KA Darling, MA Tschopp, and LJ Kecskes
Weapons and Materials Research Directorate, ARL

RK Guduru
University of Michigan

WH Yin and WH Wei
University of North Carolina

A reprint from *Acta Materialia*, Vol. 76, pp 168–185, 2014.

Approved for public release; distribution is unlimited.

List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
ARL-PDA	US Army Research Laboratory Postdoctoral Association
ARO	US Army Research Office
DOD	Department of Defense
LSMB	Lightweight and Specialty Metals Branch
MS&T	Materials Science & Technology
RDECOM	US Army Research Development and Engineering Command
SERDP	Strategic Environmental Research and Development Project
TMS	The Minerals, Metals, and Materials Society

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